

LUMINESCENCE OF REINECKE SALT AS A  
FUNCTION OF TEMPERATURE

by

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## TABLE OF CONTENTS

	Page
LIST OF TABLES . . . . .	v
LIST OF FIGURES . . . . .	vi
ABSTRACT . . . . .	vii
INTRODUCTION . . . . .	1
EXPERIMENTAL . . . . .	4
Instrumentation . . . . .	4
Chemicals . . . . .	5
Technique of Measurement . . . . .	5
RESULTS AND CALCULATIONS . . . . .	8
Quantum Yield Results . . . . .	8
Lifetime Results . . . . .	15
DISCUSSION . . . . .	22
Factors Affecting Luminescence . . . . .	22
Radiationless Transitions and Photochemistry . . . . .	23
Relationship of Quantum Yield and Lifetime . . . . .	27
REFERENCES . . . . .	29

LIST OF TABLES

Table		Page
1.	Ratios of Area to Peak Height . . . . .	8
2.	Activation Energies Obtained from $\phi$ . . . . .	13
3.	Correction for $k''$ . . . . .	21

## LIST OF FIGURES

Figure	Page
1. Photograph and Logarithmic Plot of Luminescence Decay . . . . .	6
2. Relative Quantum Yields of Reinecke Salt in 3-2-1 as a Function of Temperature and Wavelength . . . . .	9
3. Paths of Energy Degradation . . . . .	11
4. Arrhenius Plot of Relative Quantum Yields of Reinecke Salt in 3-2-1 for $\phi_0 = 20$ . . . . .	14
5. Arrhenius Plot of Relative Quantum Yields of Reinecke Salt in 3-2-1 for $\phi_0 = 14$ . . . . .	16
6. Relative Quantum Yields of Reinecke Salt in 95% Ethanol as a Function of Temperature . . . . .	17
7. Lifetime of Reinecke Salt in 3-2-1 as a Function of Temperature . . . . .	19
8. Arrhenius Plot of Lifetime of Reinecke Salt in 3-2-1 . . . . .	20
9. Comparison of Experimental and Calculated Photochemical Quantum Yields . . . . .	26

## ABSTRACT

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"LUMINESCENCE OF REINECKE SALT AS A FUNCTION OF TEMPERATURE"

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The lifetimes and quantum yields of Reinecke salt were determined as a function of temperature in a solution of methanol, water, and ethylene glycol. The activation energies and pre-exponential factors of the thermally dependent radiationless processes originating in the excited electronic states were obtained from the luminescence data. This data was compared with photochemical data on Reinecke salt in an attempt to assess the significance of the  ${}^2E_g$  electronic state in photochemical reactions.

Evidence was obtained for a thermal dependence of the radiationless transition from the  ${}^4T_{2g}$  to the  ${}^2E_g$  electronic state.

## INTRODUCTION

Transitions between excited states and also between excited states and ground states are often radiationless. An attempt to explain such radiationless transitions has been made by Gouterman (1962) in which he considers the problem as analogous to that of radiative transitions. Robinson (1961) presents a qualitative explanation of energy transfer with particular attention being paid to the crossing of potential energy surfaces and the internal degrees of freedom in a molecule.

The phenomena mentioned above and discussed by Gouterman and Robinson are purely radiationless involving only the dissipation of energy. However, there is another class of radiationless transitions which are accompanied by a chemical change in the system involved. These are photochemical reactions and they are often readily detected by a spectral change. The compounds of a number of transition metals are quite susceptible to light and a few, particularly potassium ferrioxalate, are sufficiently well characterized so that they may be used as actinometers (Hatchard and Parker 1956).

Chromium compounds are often sensitive to light and are particularly well suited to the study of photochemical deactivation because only substitution or racemization occurs, uncomplicated by other reactions. Hunt and Plane (1957), in their experiment involving the photosubstitution of hexaquo chromium(III) found a small, temperature dependent quantum yield for the reaction. As an explanation for the



data, they postulated an excited state,  ${}^2E_g$ , as the one from which photochemical reaction occurred. Schlaefer (1965) also attributed significance to the  ${}^2E_g$  state in the reaction scheme and discussed the role of this state in the photochemistry of chromium complexes in some detail. He explains that the upper excited states cannot be directly involved in the photochemical reaction since their lifetimes ( $\tau > 10^{-10} - 10^{-11}$ ) are much too short for substitution to occur. The  ${}^4T_{2g}$  (lowest excited quartet) and the  ${}^2E_g$  then remain as the possible electronic states from which reaction might occur, with the  ${}^2E_g$  being the more likely because of its longer lifetime. Edelson and Plane (1964) appeared to obtain support for the importance of the  ${}^2E_g$  state from their data on the photoaquation of hexammine chromium(III). They reported a quantum yield significantly larger than that of the hexaquo chromium(III) compound; this they attributed to the increased separation of the  ${}^4T_{2g}$  and  ${}^2E_g$  states and concomitant lowering of deactivation through the  ${}^4T_{2g}$  from the  ${}^2E_g$ . The implication was naturally that the  ${}^2E_g$  was involved in the reaction. Further justification for this implication was obtained by Wegner and Adamson (1966) when they found the quantum yield for photoaquation of hexammine chromium(III) to be essentially the same on irradiating either the  ${}^4T_{2g}$  or the  ${}^2E_g$  states.

Adamson (1959) had found, however, that  $[\text{Cr}(\text{NH}_3)_5\text{NCS}]^{+2}$  does not follow the pattern outlined by Edelson and Plane, since this compound is found to have a rather low (0.015) photochemical quantum yield, although the separation of the  ${}^4T_{2g}$  and  ${}^2E_g$  states is about as large as that in the hexammine chromium(III) compound. This finding

cast some doubt on the importance of the  ${}^2E_g$  state in the photochemical reaction.

Since the phosphorescence in chromium compounds proceeds from the  ${}^2E_g$  state it should be possible to correlate luminescence data with the photochemical data in an attempt to explain the role of the  ${}^2E_g$  state in the light induced reactions of chromium compounds. Reinecke salt was chosen for this purpose since it does luminesce, and because photochemical data for this molecule already exists. It is the primary purpose of this thesis then to attempt to associate a particular radiationless transition (as obtained from the luminescence) with photochemical reaction and also to gain further insight into the temperature dependence of radiationless transitions.

## EXPERIMENTAL

### Instrumentation

The apparatus for the determination of lifetimes consisted of: a Xenon flash lamp whose radiation passed through a Corning short pass interference filter (cutoff at approximately 650 m $\mu$ ) and a Corning 4-64 filter with maximum transmission at  $\sim$ 525 m $\mu$ ; a sample compartment with a copper cryostat; as detector, a Dumont 6911 phototube located at right angles to the exciting light. Any scattered light was prevented from entering the phototube by means of a Wratten 88A filter. The phototube signal was fed into an oscilloscope through a cathode follower probe. The lifetime of the flashlamp and electronic circuitry was calculated to be about 20  $\mu$ sec; however values of the Reinecke salt lifetimes shorter than about 70  $\mu$ sec were not used. Any further difficulties from flashlamp interference were obviated by choosing the initial intensity of the luminescence,  $I_0$ , to be some point two or three lifetimes from the origin.

Quantum yields were determined with a spectrophotofluorimeter, the detailed description of which is given by DeArmond (1963). Briefly, this consisted of a Hanovia 250W Hg-Xe lamp, a Bausch and Lomb monochromator to isolate the exciting wavelength, a sample compartment, an emission monochromator, and a Dumont 6911 phototube connected to a Heath recorder through an amplifier.

## Chemicals

Reinecke salt (AR),  $\text{NH}_4 [\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$ , was used as obtained from the Fisher Scientific Company. Reagent grade ethylene glycol and absolute ethanol were used without further purification.

## Technique of Measurement

Both the quantum yields and the lifetimes were determined with the Reinecke salt dissolved in a solvent made up of water, methanol, and ethylene glycol in the ratio 3:2:1. For brevity this solvent shall be called "3-2-1." Quantum yields were also measured in 95% ethanol.

The solution containing the Reinecke salt was placed into a cylindrical Pyrex tube; a Cu-constantan thermocouple calibrated against liquid nitrogen was lowered into the solution and the Pyrex tube was then put into the cryostat.

In the case of lifetime measurements, it was found advantageous to cool the cryostat by adding, successively, small amounts of liquid nitrogen. The heat transfer was sufficiently slow to allow the emission to be examined at approximately ten temperatures in any individual experiment. The voltage from the thermocouple was measured with a Leeds and Northrup potentiometer, while the emission curve produced on the oscilloscope was photographed with a Polaroid Oscilloscope Camera using 200 speed film. An example of the emission curve and its logarithmic plot is shown in Figure 1.

For the quantum yields, the sample was placed in a pre-cooled cryostat. This technique gave a rather good glass which showed very

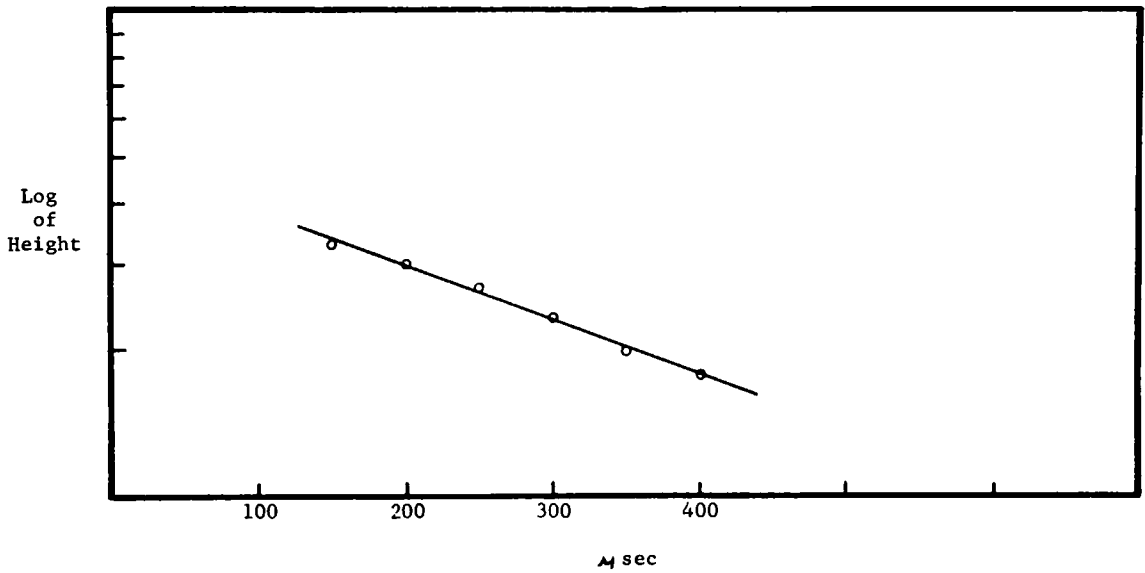
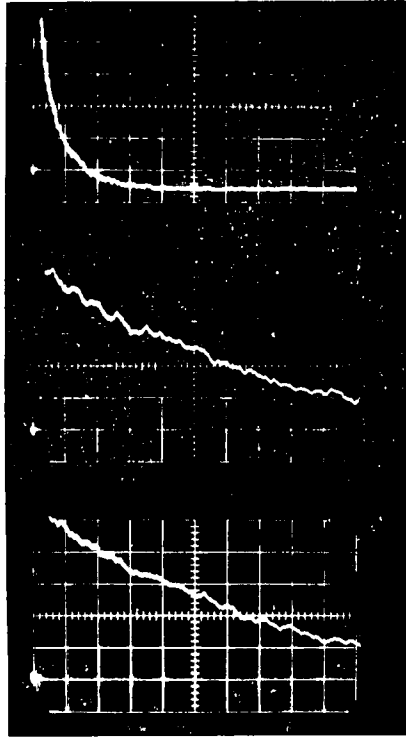


Figure 1. Photograph and Logarithmic Plot of Luminescence Decay

little cloudiness and in which cracking occurred only after the quantum yield began levelling off. Temperatures were measured as for lifetimes. Since the emission monochromator was set at the emission peak for the Reinecke salt phosphorescence, a smooth curve representing the relative quantum yield as a function of temperature was produced on the recorder. A phototube in line with the light source and sample was used to monitor the light intensity and to check the quality of the glass. Visual observations of the glass were also made from time to time by removing the phototube.

## RESULTS AND CALCULATIONS

### Quantum Yield Results

In the determination of quantum yields it was found possible to use the peak height of the emission as a measure of the quantum yield since the ratio of curve area to peak height was constant at all temperatures as shown by the following table.

TABLE 1  
RATIOS OF AREA TO PEAK HEIGHT

Temp. °K	area/peak height	% deviation from mean
187	1.55 sq cm/cm	0.0
166	1.57 sq cm/cm	1.3
135	1.53 sq cm/cm	1.3

Periodic checks were made by measuring the area under the emission curve with a planimeter, and the results were found to agree with those obtained by using the ratio to calculate the quantum yields.

Experiment showed that oxygen did not affect the luminescence, and so further experiments were performed without degassing.

The luminescence also showed no change with exciting wavelength as indicated by the various curves plotted in Figure 2. These curves are seen to be in good agreement to about 180 °K, at which point a certain amount of irreproducibility occurs and the data becomes somewhat scattered. In order to obtain the superposition of

△ ○ □ ● exciting wavelength is 365 mμ

▲ exciting wavelength is 546 mμ

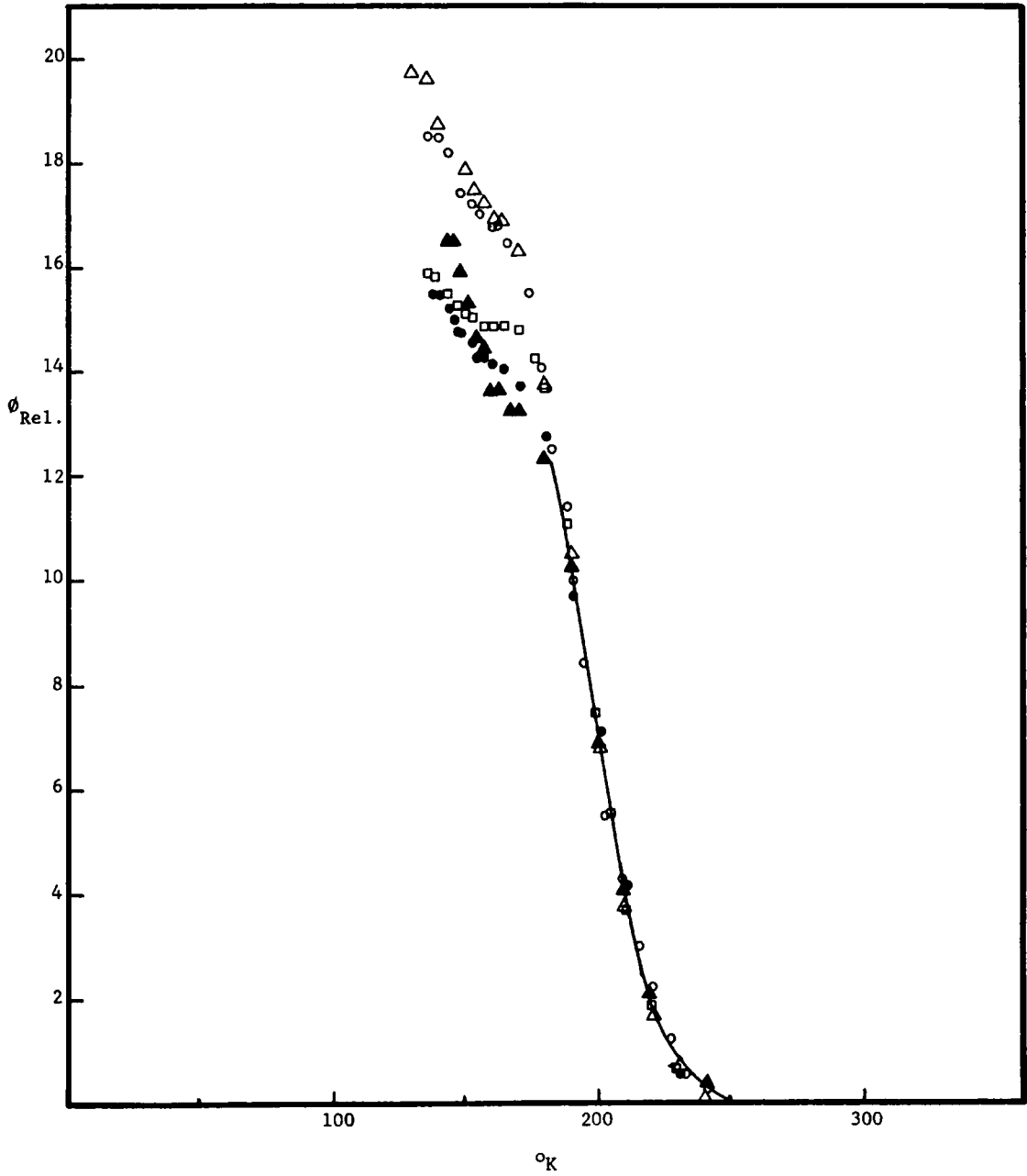


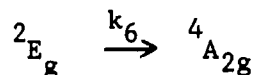
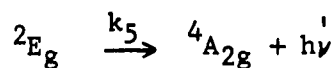
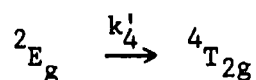
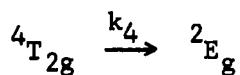
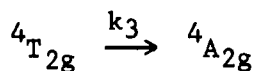
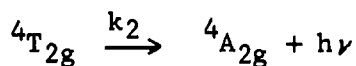
Figure 2. Relative Quantum Yields of Reinecke Salt in 3-2-1 as a Function of Temperature and Wavelength



the curves in Figure 2, one curve was chosen as a basis and all other curves were scaled to this one.

The Cr(III) energy levels involved in the luminescence of Reinecke salt are shown in Figure 3. The solid and broken lines indicate radiative and non-radiative transitions respectively. Energy levels above the  ${}^4T_{2g}$  are not included since higher excited states rapidly convert to the  ${}^4T_{2g}$  and are not of importance in the case of Reinecke salt (Chatterjee and Forster 1964).

The processes of interest which occur after excitation can be expressed as follows:



By invoking the steady state approximation and the definition of the phosphorescence quantum yield, the above expressions can be combined to give one involving only the phosphorescence quantum yield and the rate constants. For the  ${}^4T_{2g}$  state

$$1) \quad \frac{d[{}^4T_{2g}]}{dt} = I - [k_2 + k_3 + k_4][{}^4T_{2g}] + k'_4[{}^2E_g] = 0$$

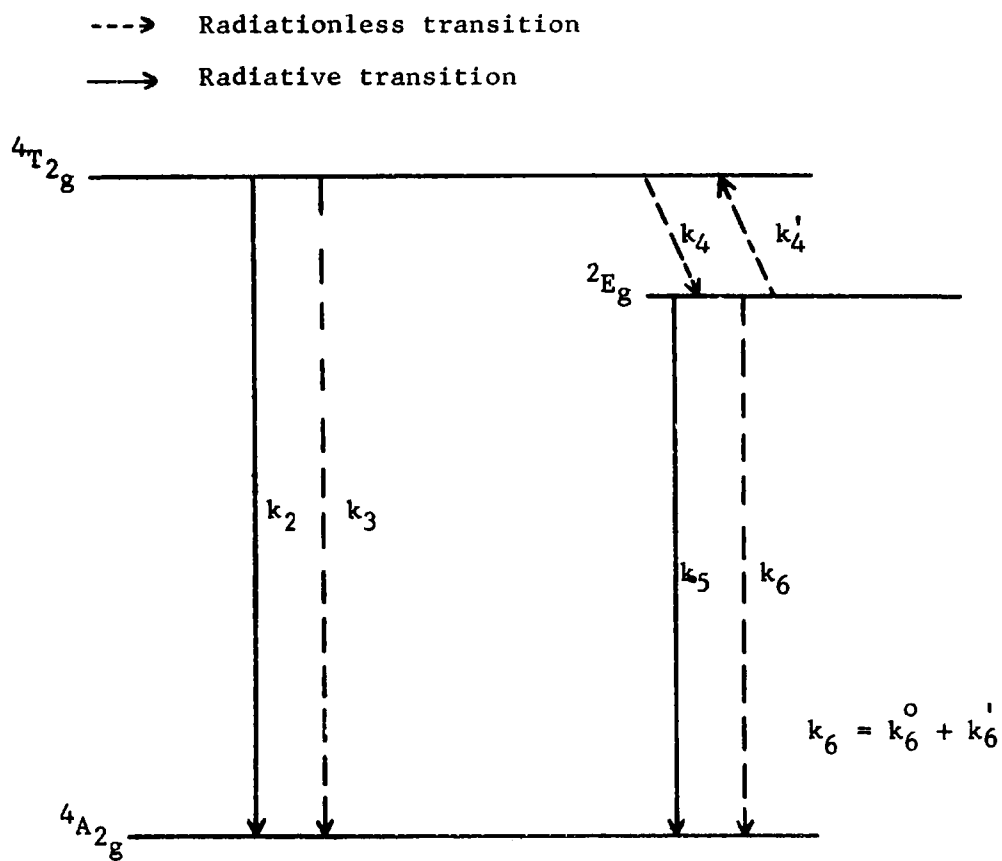


Figure 3. Paths of Energy Degradation

and for the  ${}^2E_g$  state

$$2) \quad \frac{d [{}^2E_g]}{dt} = k_4 [{}^4T_{2g}] - [k'_4 + k_5 + k_6] [{}^2E_g] = 0$$

The phosphorescence quantum yield is defined as

$$3) \quad \phi = \frac{k_5 [{}^2E_g]}{I} \quad \text{where } I \text{ is the intensity absorbed.}$$

Substituting for I in equation 1 gives

$$4) \quad k_5 \frac{[{}^2E_g]}{\phi} = [k_2 + k_3 + k_4] [{}^4T_{2g}] - k'_4 [{}^2E_g]$$

and

$$5) \quad \frac{1}{\phi} = \frac{[k_2 + k_3 + k_4] [{}^4T_{2g}]}{k_5 [{}^2E_g]} - \frac{k'_4}{k_5}$$

Equation 2 can be solved to give  $[{}^4T_{2g}] / [{}^2E_g]$  and on substituting for this ratio into equation 5, one obtains the following expression:

$$6) \quad \frac{1}{\phi} = \frac{[k_2 + k_3 + k_4] [k'_4 + k_5 + k_6]}{k_4 k_5} - \frac{k'_4}{k_5}$$

Equation 6 can be simplified if it is assumed that 1)  $k_2$  and  $k_5$  are independent of temperature as is common for radiative transitions, 2)  $k_4$  is independent of temperature, 3)  $k_6$  is composed of a temperature independent,  $k_6^0$ , and a temperature dependent part,  $k_6'$  which becomes negligible at sufficiently low temperatures. These assumptions imply that there is a limiting value of the relative quantum yield,  $\phi_0$ , given by the following expression:

$$7) \quad \frac{1}{\phi_0} = \frac{[k_2 + k_3 + k_4] [k_5 + k_6^0]}{k_4 k_5}$$

and that the temperature dependent transition (below 170 °K) will be given by:

$$8) \quad \frac{1}{\phi} - \frac{1}{\phi_0} = \frac{[k_2 + k_3 + k_4] k_6'}{k_4 k_5} = \tau k_6' = s_1 e^{-E/RT}$$

The validity of choosing a limiting quantum yield is borne out by the levelling off of the luminescence intensity at low temperatures. Thus temperature dependent constants for the radiationless transitions from the  $^2E_g$  to the ground state can be obtained from the quantum yields. An Arrhenius plot, Figure 4, in which  $\ln ck'_6$  is plotted versus  $1/T$  °K suggests that two temperature dependent processes are involved in the transition. Activation energies for the transitions are obtained from the slopes in Figure 4. Further justification for the implication that  $k'_6$  involves two processes will be provided by the lifetime data.

Since there was a certain amount of irreproducibility in the low temperature portion of the quantum yield curves, an exact value for  $\phi_0$  could not be chosen; because of this several values were selected and calculations and plots were made using these values. The activation energies obtained from these calculations are included in Table 2.

TABLE 2  
ACTIVATION ENERGIES OBTAINED FROM  $\phi$

$\phi_0$	$E_1$	$E_2$	$E_2$ (corrected)
14	5 kcal/mole	7.7 kcal/mole	9.7 kcal/mole
16	4.7 kcal/mole	7.0 kcal/mole	9.56 kcal/mole
18	3.4 kcal/mole	6.4 kcal/mole	7.64 kcal/mole
20	3.56 kcal/mole	5.8 kcal/mole	6.75 kcal/mole

As will also be seen in the lifetime results, the process associated with  $E_1$  contributes a small amount to the curve in the intermediate

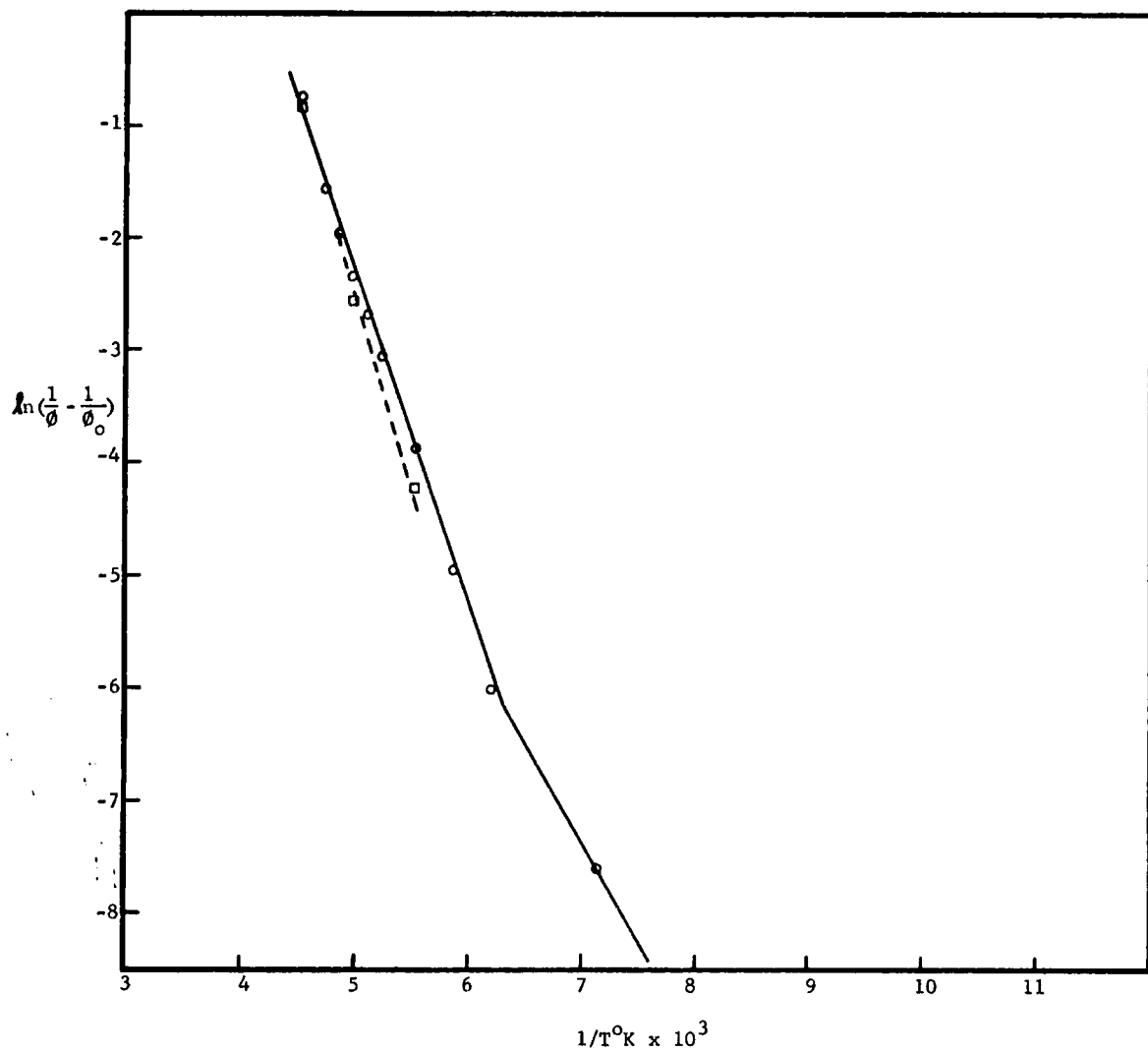


Figure 4. Arrhenius Plot of Relative Quantum Yields of Reinecke Salt in 3-2-1 for  $\phi_0 = 20$

temperature regions. A correction was made for this contribution by evaluating  $ck_6'$  in this region and entering the results into the following equation:

$$9) \quad \frac{1}{\phi} - \frac{1}{\phi_0} = \frac{[k_2 + k_3]}{k_4 k_5} k_4' + ck_6'$$

Since the quantum yield involves a transition from the  ${}^4T_{2g}$  state, the two terms on the right in equation 9, may involve thermal processes from this state. The corrected constant for the process associated with  $E_2$  is then given by:

$$10) \quad \frac{1}{\phi} - \frac{1}{\phi_0} - ck_6' = \frac{[k_2 + k_3]}{k_4 k_5} k_4'$$

These corrections are entered in Table 2 above, while Figures 4 and 5 show the corrections plotted for two different values of  $\phi_0$ .

The curve in Figure 6 represents the relative luminescence quantum yield of Reinecke salt in ethanol. The effect of environment is readily noticeable since the temperature at which luminescence begins is lower than in 3-2-1. Calculation of activation energies from an estimated limiting quantum yield showed them to be quite different from those found in 3-2-1.

### Lifetime Results

Experimentally the lifetime is obtained from the exponential oscilloscope trace of the  ${}^2E_g$  emission of Reinecke salt by using the equation:

$$11) \quad I = I_0 e^{-t/\tau}$$

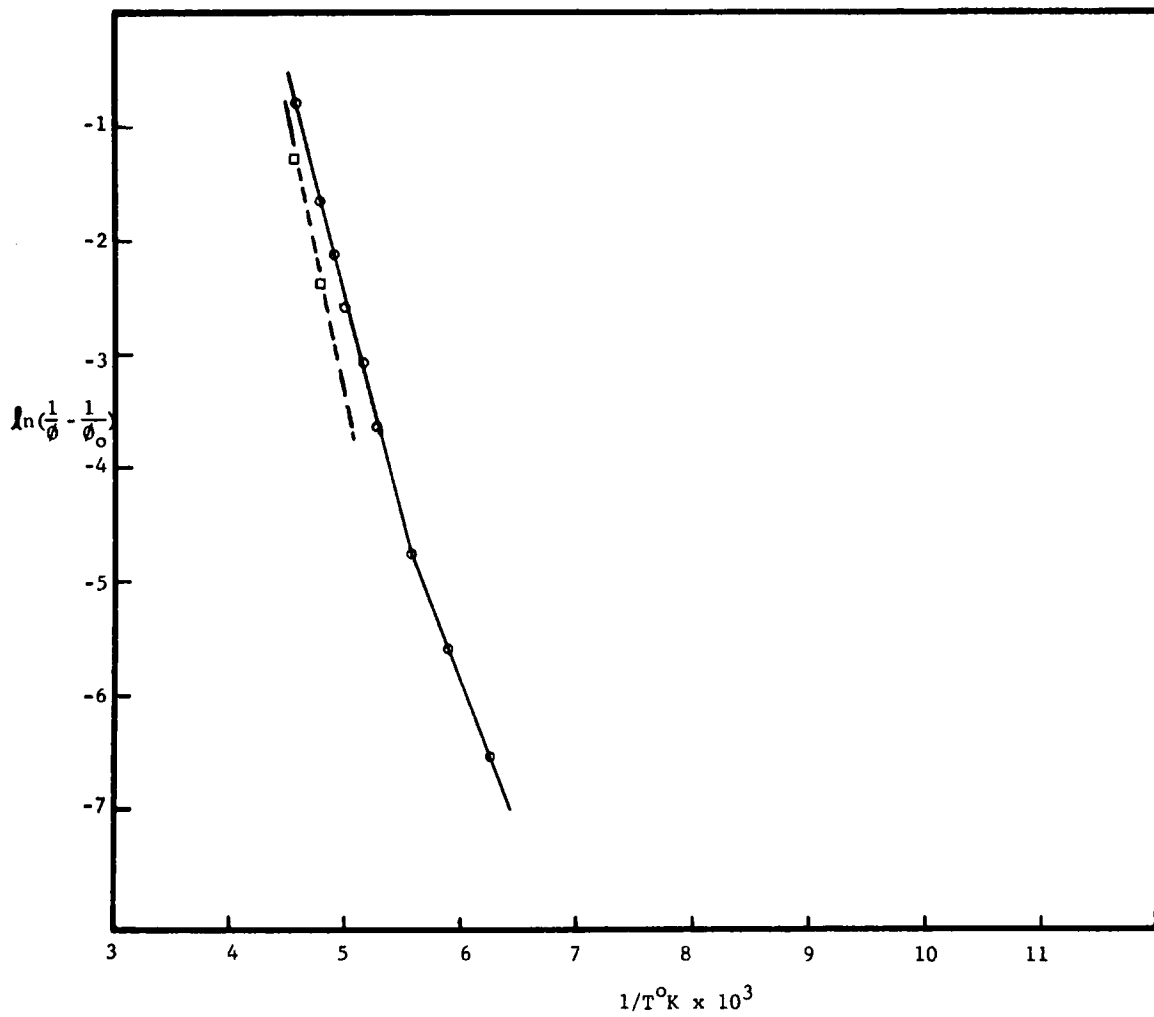


Figure 5. Arrhenius Plot of Relative Quantum Yields of Reinecke Salt in 3-2-1 for  $\phi_0 = 14$

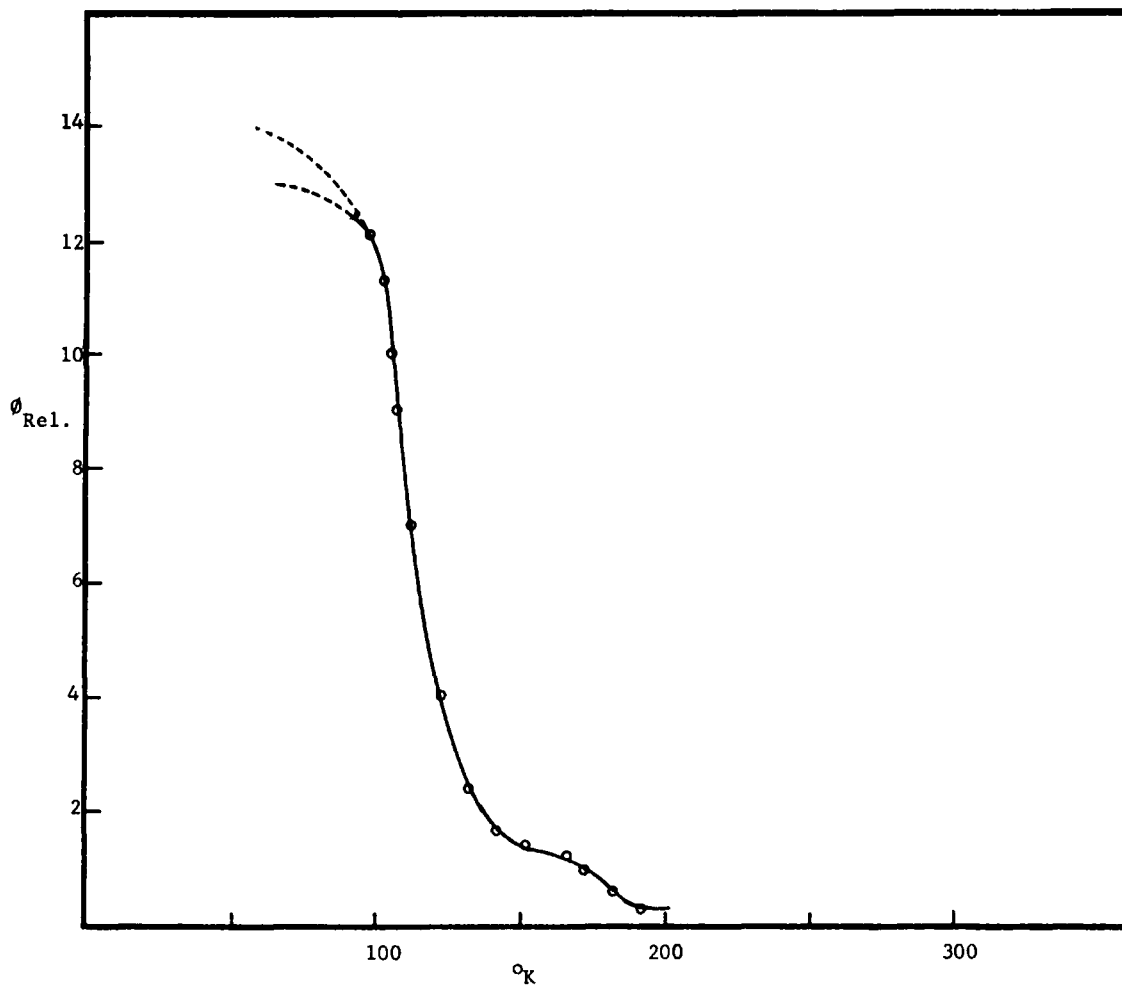


Figure 6. Relative Quantum Yields of Reinecke Salt in 95% Ethanol as a Function of Temperature



where  $I_0$  is the initial intensity and  $I$  is the intensity at time  $t$ . A plot of lifetimes so obtained versus temperature is shown in Figure 7.

Theoretically the lifetime of the  ${}^2E_g$  state is equal to the reciprocal of the sum of the constants for the radiative and radiationless transitions which depopulate the state. The assumptions made for the quantum yields apply also to the lifetimes, and a limiting value of the lifetime is chosen such that the following equation results:

$$12) \quad \frac{1}{\tau} - \frac{1}{\tau_0} = [k_5 + k_6^0 + k_6'] - [k_5 + k_6^0] = k_6'$$

where  $k_6'$  includes all thermal radiationless processes originating in the  ${}^2E_g$  state. After applying equation 12 to the lifetime data, the results were plotted as  $\ln k_6'$  vs  $1/T$ . The Arrhenius plot (Fig. 8) shows that  $k_6'$  is actually composed of two thermal processes,  $k''$  and  $k'''$ . Since the numbers obtained for lifetimes are absolute rather than relative, as in the case of quantum yields, the pre-exponential factors as well as the activation energies can be calculated from the Arrhenius plot. In the higher temperature region both processes are operative and the initial plot of  $k'''$  (associated with  $E_2$ ) contains a contribution from  $k''$  (associated with  $E_1$ ). The correction for this contribution was made by calculating  $k''$  at several intermediate temperatures and substituting these values into the following equation which was then solved for  $k'''$ :

$$13) \quad \frac{1}{\tau} - \frac{1}{\tau_0} = k_6'' + k_6'''$$

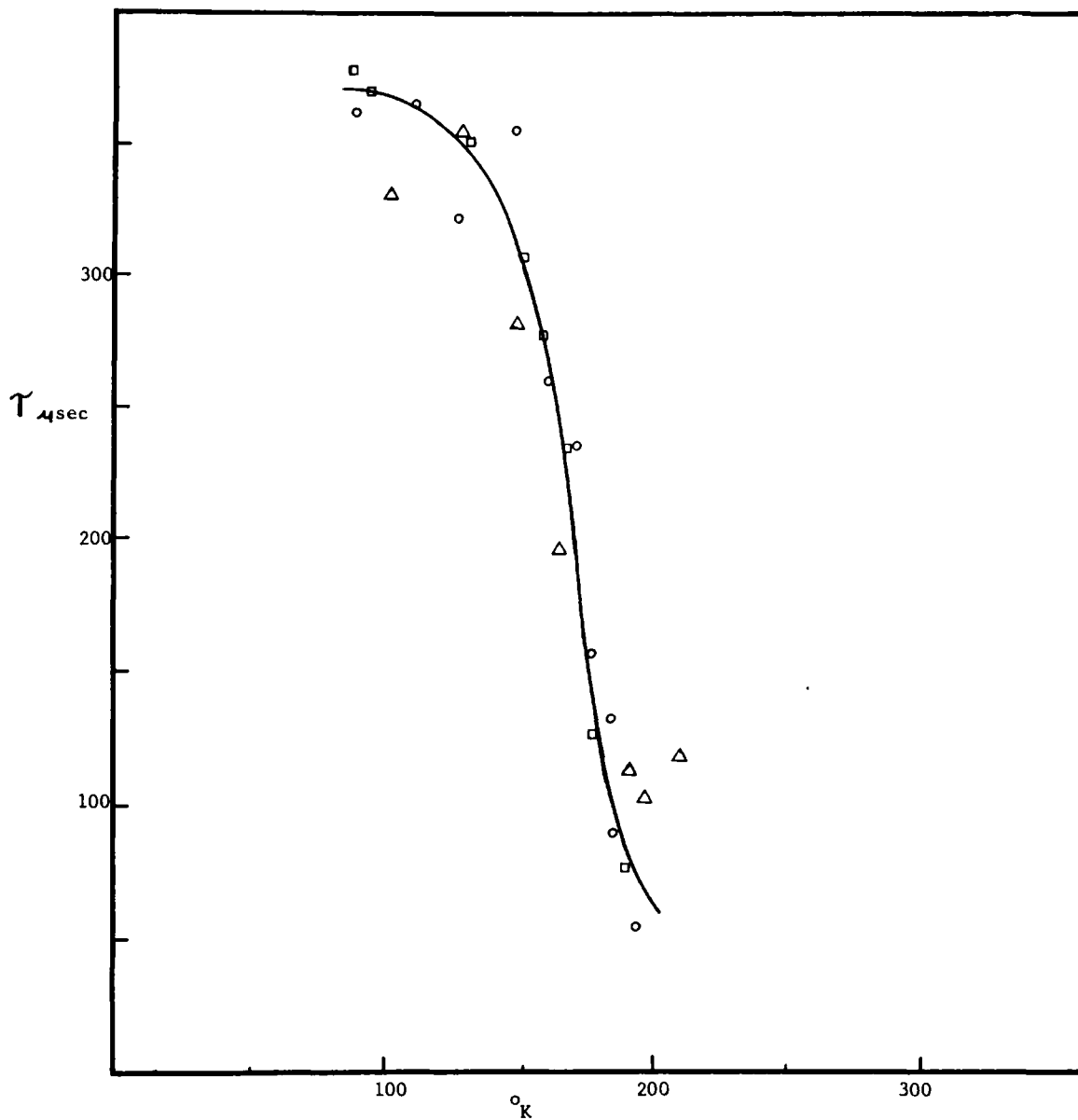


Figure 7. Lifetime of Reinecke Salt in 3-2-1 as a Function of Temperature

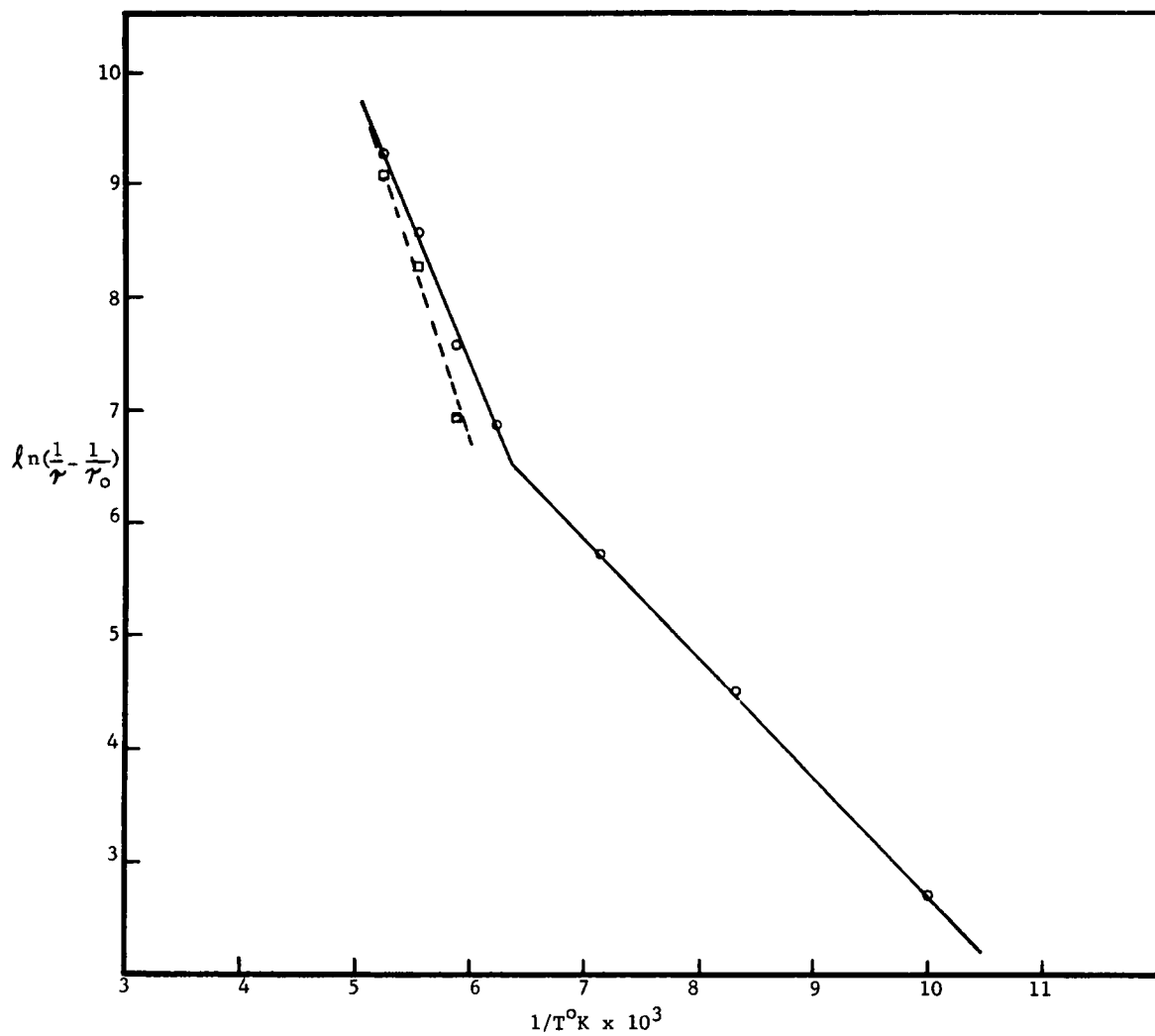


Figure 8. Arrhenius Plot of Lifetime of Reinecke Salt in 3-2-1

The table below generally illustrates how the corrections are made, and the dashed line in Figure 8 shows them incorporated into the graph.

TABLE 3  
CORRECTION FOR  $k''$

T °K	1/T x 10 <sup>3</sup>	$(\frac{1}{T} - \frac{1}{T_0})$	$k''$	$k'''$	
				$(\frac{1}{T} - \frac{1}{T_0} - k'_6)$	ln(k''')
170	5.89	1.892x10 <sup>3</sup>	9.10x10 <sup>2</sup>	9.82x10 <sup>2</sup>	6.89
180	5.56	5.115x10 <sup>3</sup>	1.28x10 <sup>3</sup>	3.84x10 <sup>3</sup>	8.25
190	5.26	10.46x10 <sup>3</sup>	1.75x10 <sup>3</sup>	8.71x10 <sup>3</sup>	9.07

The pre-exponential factors and activation energies obtained from the lifetime data are:

$$S_1 = 4.47 \times 10^5 \text{ sec}^{-1}$$

$$E_1 = 2.09 \text{ kcal/mole}$$

$$S_2 = 5.25 \times 10^{10} \text{ sec}^{-1}$$

$$E_2 = 5.96 \text{ kcal/mole}$$

## DISCUSSION

### Factors Affecting Luminescence

As mentioned in the previous section, the luminescence quantum yields were found to be independent of exciting wavelength. This indicates that upper excited states undergo a rapid conversion to the lowest excited state rather than to the ground state. Thus the model proposed earlier, showing transitions only from the  ${}^2E_g$  and  ${}^4T_{2g}$  states, appears to be appropriate for dealing with the various depopulations occurring in Reinecke salt.

The luminescence was strongly affected by environment as indicated by the considerably lower temperature at which phosphorescence appeared when Reinecke salt was dissolved in 95% ethanol (Fig. 6). The effect of environment on luminescence was studied by Targos (1966) who noted that in  $Cr(aca)_3$  glasses luminescence was apparently associated with solvent viscosity. In the case of Reinecke salt dissolved in ethanol, a rapid increase in luminescence occurs near  $140^\circ K$ , whereas in 3-2-1, a rapid increase occurs near  $200^\circ K$ . Though no actual viscosity measurement was attempted, visual observation of the two systems at temperatures near  $200^\circ K$  showed 3-2-1 to be quite viscous while ethanol had lost little of its room temperature fluidity.

It is interesting to note that though the  ${}^2E_g$  to  ${}^4A_{2g}$  transition is spin-forbidden, a large pre-exponential factor,  $10^{10}$  (determined from lifetime data), was found to be associated with  $k'''$ ; this

result is similar to that encountered by Targos (1966) for the crystal system,  $\text{Cr}(\text{aca})_3$  dissolved in  $\text{Al}(\text{aca})_3$ .

### Radiationless Transitions and Photochemistry

The Arrhenius plot of the lifetime data has shown clearly that  $k'_6$  is actually composed of two thermally dependent radiationless transitions, and as indicated earlier  $k'_6$  contains in it all possible radiationless processes depopulating the  ${}^2E_g$  state whether they occur directly to the ground state or to an upper state and then to the ground state. The activation energies obtained for the radiationless processes are 2.09 kcal ( $E_1$ ) and 5.96 kcal ( $E_2$ ). The problem is to associate these activation energies with a definite depopulation mechanism. Several possibilities present themselves. These are: 1) depopulation in which both transitions occur directly to the ground state, 2) depopulation through the  ${}^4T_{2g}$  state via thermal excitation from the  ${}^2E_g$ , or 3) depopulation by means of a photochemical decomposition.

For the second case, the activation energy of the transition and the separation of the  ${}^4T_{2g}$  and  ${}^2E_g$  states must be considered. The absorption maxima of the  ${}^4T_{2g}$  and  ${}^2E_g$  transitions in Reinecke salt occur at  $1.92 \times 10^4 \text{ cm}^{-1}$  and  $1.34 \times 10^4 \text{ cm}^{-1}$  respectively (Adamson 1966), a difference of about 16 kcal. Though this energy does not represent the true separation of the two states, it does not appear that this separation will be as much as 10 kcal less. In the case of the chromium acetylacetonates, Targos (1966) argued that deactivation of the  ${}^2E$  might take place through the  ${}^4T_2$ ; the activation energy

(7.3 kcal) he associated with this process made this hypothesis possible. For Reinecke salt, however, the activation energy is 5.96 kcal, a value that is probably an outside limit to the energy separating the  ${}^4T_{2g}$  and  ${}^2E_g$  states. It appears then that depopulation through the  ${}^4T_{2g}$  is not significant.

Depopulation of the  ${}^2E_g$  state by a photochemical mechanism has been suggested by several authors, with Edelson and Plane contending that the quantum yields are a function of the energy gap between the  ${}^2E_g$  and  ${}^4T_{2g}$  states. If the  ${}^2E_g$  state is in fact the photochemically reactive state, then it should be possible to establish one of the radiationless transitions from this state as responsible for the reaction.

In his study of the photoaquation of Reinecke salt, Adamson (Private Communication) found activation energies of 2.3 and 0.55 kcal associated with the substitution reaction. Comparison of these with the activation energies obtained from luminescence leads to the conclusion that  $k'''$  (associated with  $E_2$ ) cannot be responsible for photochemical decomposition since the activation energy (5.96 kcal) for  $k'''$  is too high to be related to either of the photochemically obtained activation energies. It will be noted, however, that the larger activation energy as determined photochemically is quite close in value to  $E_1$  (2.09 kcal) as obtained from the lifetimes. If it is assumed that  $k''$  (associated with  $E_1$ ) is responsible for the photo-substitution, then the quantum yield upon irradiating only the  ${}^2E_g$  state should be  $\frac{k''}{\Sigma k}$ , where the denominator contains all  ${}^2E_g$  depopulating processes. Since  $\Sigma k$  is equal to  $1/\tau$ , the quantum yield is

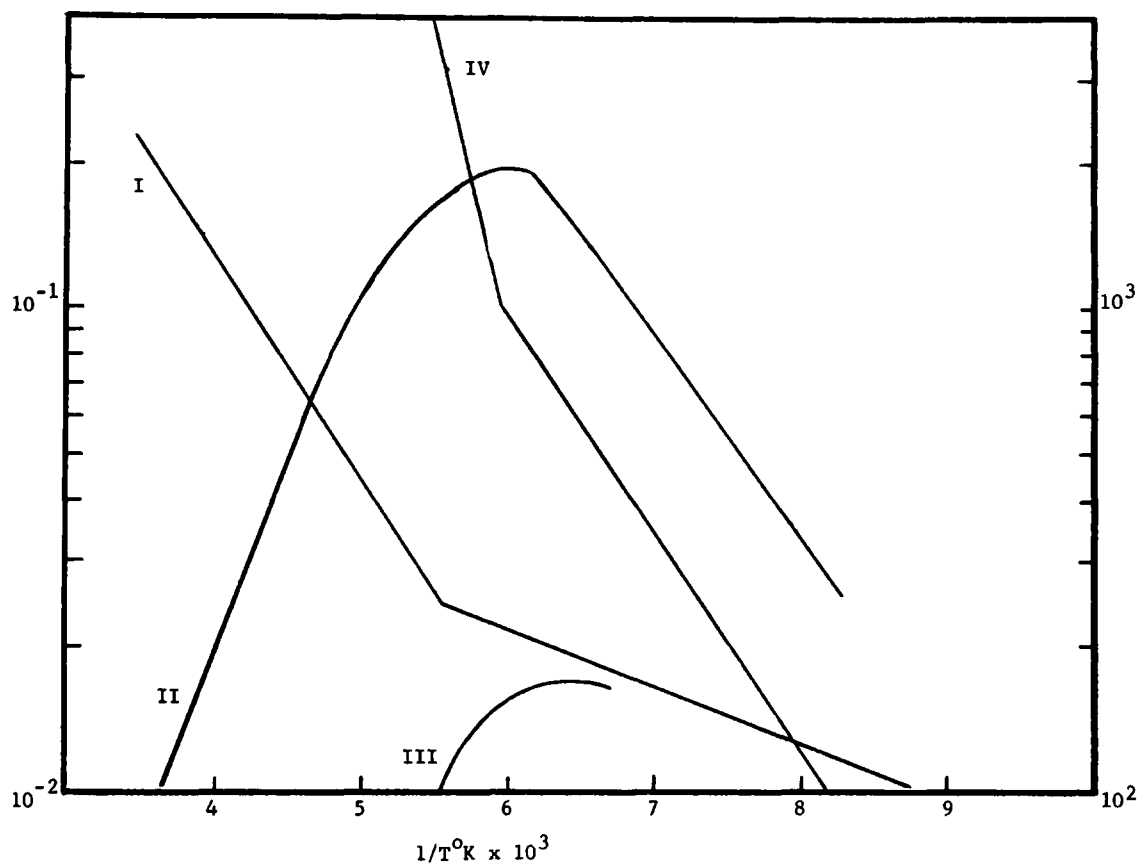
given by  $k''\tau$ . A plot of the photochemical quantum yields calculated on the basis of the foregoing assumptions is compared with Adamson's experimental data in Figure 9. In the higher temperature region, the significant point is that the slopes for the calculated and experimental quantum yields are different in sign. This, in addition to the fact that the quantum yields become very different as the temperature increases (above 250°K) eliminates  $k''$  as a significant path for photosubstitution at these temperatures. The calculated and experimental quantum yields are also quite different in the low temperature region, and on these grounds  $k''$  would seem to be eliminated as a possible photochemical transition. In addition it should be mentioned that the calculated quantum yield was made on the assumption that only the  ${}^2E_g$  state was being irradiated, whereas the actual photochemical reaction occurs after excitation to the  ${}^4T_{2g}$  state. Data seems to indicate that conversion from the  ${}^4T_{2g}$  to the  ${}^2E_g$  is thermally dependent, which simply means that the slope of the calculated quantum yield should actually be more negative than it is, further strengthening the argument that  $k''$  does not lead to photosubstitution.

The question remains as to whether there might be some process,  $k''''$ , too small to be detected in luminescence experiments, that is responsible for the photochemistry. In order to answer this question such a constant was calculated using the following equation:

$$14) \frac{\phi}{\tau} = k'''' = Se^{-\frac{Ea}{RT}}$$

The activation energy (0.55 kcal) and quantum yield (0.02) were chosen from Adamson's data, while the lifetime was obtained from our data.





- I Adamson's experimental quantum yield
- II Calculated quantum yield using  $k''$
- III Calculated quantum yield using  $k''''$
- IV  $\lambda^n \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right)$

Figure 9. Comparison of Experimental and Calculated Photochemical Quantum Yields

After calculating the pre-exponential factor ( $3.5 \times 10^2 \text{ sec}^{-1}$ ) using equation 14, several values of  $k''''$  and then of  $\phi_{aq}$  were calculated on the assumption that  $k''''$  was responsible for the photoreaction. The results are shown as curve III in Figure 9. Again the slopes are seen to be of different sign, thus eliminating this last possibility as a path for photochemical reaction. In view of these facts, the temperature dependent processes depopulating the  ${}^2E_g$  state in Reinecke salt appear to be purely radiationless transitions going directly to the ground state.

#### Relationship of Quantum Yield and Lifetime

If the lifetime and quantum yields are compared at various temperatures, it is readily seen that the lifetime falls off more rapidly than the quantum yield; this suggests that a mechanism is acting to increase the number of molecules in the  ${}^2E_g$  state even as the thermally dependent radiationless transitions from this state are increasing. This mechanism appears operative below  $160^\circ\text{K}$ , where the  $\phi/\tau$  ratio would be given by  $\frac{k_4 k_5}{k_2 + k_3 + k_4}$ . The constant for intersystem crossing,  $k_4$ , is the only likely candidate for affecting the  $\phi/\tau$  ratio, since  $k_2$  and  $k_3$  should not decrease and  $k_5$  is not expected to increase with temperature. The data is meager and somewhat uncertain but the activation energies from the quantum yields and lifetimes may support the contention that  $k_4$  contains a thermally dependent portion.

The activation energies determined from the quantum yields lie within the range 3.4 - 5 kcal/mole for  $E_1$  and 6.75 - 9.7 kcal/mole for  $E_2$  (corrected); the  $E_1$  and  $E_2$  values obtained from lifetime data are

2.09 and 5.96 kcal/mole respectively. It is evident that the activation energies determined from lifetimes do not lie within the range of values obtained from the quantum yield data, nor does there seem to be any valid reason for extending the range of quantum yield values to include these activation energies. The conclusion then is that some portion of the activation energies obtained from quantum yields actually represents a thermal mechanism not operative in the transitions determining the lifetime.

The conclusion reached above brings with it the question as to why a temperature dependent mechanism is apparent in some cases and not in others. It may simply be that in systems with a small  $k_4$  the dependence would appear while in systems where  $k_4$  is large no temperature dependence would be evident. Comparison, in several compounds, of activation energies determined from quantum yields and lifetimes might shed some light on this question.

## REFERENCES

- Adamson, A. W., J. Inorg. Nucl. Chem. 13, 275 (1960).
- Adamson, A. W., J. Inorg. Nucl. Chem. 28, 1955 (1966).
- Adamson, A. W., Private Communication.
- Chatterjee, K. K. and Forster, L. S., Spectrochim. Acta 20, 1603 (1964).
- DeArmond, K., Dissertation, University of Arizona (1963).
- Edelson, M. R. and Plane, R. A., J. Phys. Chem. 63, 327 (1959).
- Gouterman, M., J. Chem. Phys. 36, 2846 (1962).
- Hatchard, C. G. and Parker, C. A., Proc. Roy. Soc. (London), A235, 518 (1956).
- Plane, R. A. and Hunt, J. P., J. Am. Chem. Soc. 79, 3343 (1957).
- Robinson, G. W., J. Molec. Spec. 6, 58 (1961).
- Schlaefter, H. L., J. Phys. Chem. 69, 2201 (1965).
- Targos, W. M., Thesis, University of Arizona (1966).
- Wegner, E. E. and Adamson, A. W., J. Am. Chem. Soc. 88, 394 (1966).