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Kinetic of the Fading Reaction of  $\alpha_1$ -Salicylidene Aniline in Ethanol

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# Kinetic of the Fading Reaction of $\alpha_1$ -Salicylidene Aniline in Ethanol\*

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#### ABSTRACT

Salicylidene Aniline originally crystallized from a solution has lemon yellow colour. Irradiation with near ultra violet causes the color to change from yellow to red. The red state changes spontaneously back to yellow this change is accelerated by visible light. Kinetic data are reported in the temperature range between 18,5 and 55°C, for the dark fading reactions of the colored isomers formed by the ultra violet irradiation. First order reactions are observed, Activation energies and entropies of activation are reported.

#### INTRODUCTION

Photochromic organic systems, in which a visible coloration induced by ultra violet irradiation can be reversibly eradicated (thermally or photochemically) have been known for a long time and extensively reviewed (1). A red coloration due to a band at 480 nm., develops when crystals of salicylidene aniline are irradiated in the ultra violet a reversible bleaching can be carried out thermally or by illumunation with blue light the phenomenon was readily explained in terms of the light-induced equilibrium.

Most of the information on the anil systems is due to the recent investigations (2) showed that the ortho-OH group is an essential

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condition for photochromism. Salicylidene aniline undergoes a photochemical isomerization involving the displacment of a hydrogen atom from the 0-hydroxy group to the bridge nitrogen atom and geometrical changes in the molecular framework.

$$C = N$$

$$h \cdot (uv)$$

$$h \cdot (vis) or \triangle$$

$$C - NH$$

Salicylidene aniline is particularly interesting because it can be prepared in two strongly photochromic crystalline forms and also in a nonphotochromic form. The two crystalline forms require similar energy for inducing the 480 nm band, but differ markedly in energy for the reverse change and in the kinetics of spontaneous fading. Recently (3) with the help of flash techniques, the reaction has also been observed in fluid solutions.

#### EXPERIMENTAL

Salicylidene aniline was prepared by warming equimolar quantities of aniline and salicylaldehyde in ethanol and allowing the solution to cool. The product was purified by repeated recrystallization from ethanol until further recrystallization produced no further changes in melting point, x-ray diffraction pattern or other properties. This compound crystallized form alcohol as yellow granules, the choice of solvent affected only the crystal habit, the crystal structure was the same, with different solvents. The above procedure gave the crystalline form of salicylidene aniline (this will be called α<sub>1</sub>-Salicylidene aniline), α<sub>2</sub>-form does not usually spontaneously crystallize from solution or from a melt, on several occasions small amounts of this form crystallized from nonpolar solvent, along with larger amounts of the  $\alpha_1$  form. Selected portions of this a, form were used to seed other solutions or supercooled melts so as to prepare larger quantities of this crystalline phase. Both α1 and α, forms have a melting point of 50.5°C and a density of 1.18 gm/cm<sup>3</sup>. The forms may be readily distinguished by their x-ray diffraction patterns. Crystallographic data have been reported by Cohen et al (4). A third crystalline form was prepared by the procedure used by Ebara (3). Orange crystals were

obtained by crystallisation from ethanol or n-heptane below 6°C. These crystals were not photochromic but fluoresced strongly under 365 nm., radiation, they suggest that this variety be called the  $\beta$ -form of salicylidene aniline.

α1 -Salicylidene aniline was purified by repeated recrystallisation in the dark. The solutions were prepared in "Low actinity" flasks in order to prevent any photo conversion by room light, and allowed to stand in the dark overnight before the experiments then the solution was placed into a 20 cm., long double-walled quartz vessel which has oplically flat end windows and with a surrounding outer jacket containing a liquid filter (0.75 gram iodine in 100 cc, CCl<sub>4</sub>) one cm in thickness. Temperature gradients in the cell were avoided by circulating the filter solution through a thermostated bath by means of an all glass system, through the reaction vessel's outer jacket to act as an ultra violet cut-off filter and to thermostate the sample in the temperature range  $10\,\mathrm{to}\,60\,^{\circ}\mathrm{C}$ In order to get rid of the stray light, the ends of the reaction cell were shielded with blackened light hoods. An electrical energy of approximately 1125 joules (10µ F, 15 kV.) was discharged through the air filled flash lamps. Absorption of the flash at 480 nm., was followed photoelectrically, changes in the detector signal occuring during a single sweep were recorded on a Tektronix, 535-A type oscilloscope with a Battie Oscillatron Camera (BC1, k-5) using 3000 Asa, type 47 roll film. The monitoring light source was an atlas 100 watts quartz iodine lamp with a Kodak-Wratten filter (Transmitting above 410 nm.,) placed between the iodine lamp and the reaction cell, to protect the sample from ultra violet radiation. The temperature of the solution was measured to within  $\pm~0.05\,^{\circ}\mathrm{C}$ by the temperature monitoring circuit. No temperature rise greater than 0.1°C following the flash was observed.

#### PROCEDURE AND RESULT

Solutions of  $3.5 \times 10^{-4}$  molar  $\alpha_1$ -Salicylidene aniline in spectroscopically pure ethyl alcohol was flashed at the following temperatures 18.5, 19.2, 23.5, 27.0, 31.7, 36.3, 39.4, 41.2, 46.8, 53.0, 55.0 °C. The concentration was chosen as the lowest convenient value for which the resulting concentrations of transient species gave

oscilloscope signals well in excess of the noise level for photoelectric recording at 480 nm. The reaction was followed for at least three half-lives. Typical results are shown in figure 1., which portrays the oscilloscope traces of the decay of the transient species at 480 nm., at the temperatures indicated. From such data first order plots were constructed Table I, where A is absorbance at any time,  $A_{\infty}$  is the final absorbance and t is the decay time. The rate constant "k" at each temperature was calculated using a computer program from the numerical values of I and time at each temperature (figure 1), where I is the distance from any point of the oscilloscope trace to the line of zero percent transmission. From these values a plot of log k versus 1/T Table II led to the calculation of activation energy. And the entropy change was obtained using the following equation.

$$k \, = \, e \, \, . \, \frac{\overline{k} \, T}{h} \, \, . \, e^{-E_{exp}/_{RT}} \, \, . \, e^{\Delta S^* / \, R} \label{eq:k_exp}$$

 $\Delta S^*$  is calculated at 30°C. The fading reaction of  $\alpha_i$ -Salicylidene Aniline was shown to follow first order kinetic with the observed parameters.  $\Delta S^*=11.4040$  e. u. and  $E_a=10.3640$  kcal/mole figure 2, shows the absorption of the filter solution plotted transmittance versus wavelength by using "Unicam-SP-600" spectrophotometer.

#### DISCUSSION

Polar nonaqueous solutions of salicylideneaniline exhibit an additional weak band around 450 nm., with absorbance amounting to a few percent of that of the 340 nm. band, Such an effect has been previously observed (5), and attributed to low concentration of a tautomeric species of salicylideneaniline. The effect of water can be understood if one recalls that intermolecular hydrogen bonds with alcohol and other nonaquous solvents are much weaker than with water molecules (6), (7). The addition of water to the anil alcoholic solution will introduce solvent molecules which efficiently compete with the intermolecular O-H...N bridge leading to its rupture. The resulting molecular species is unbridged and its spectrum resembles that of other unbridged anils such as the

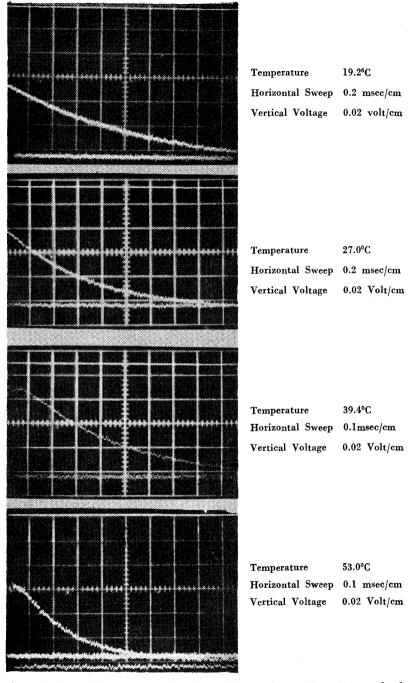


figure 1: The oscilloscope traces of the decay of the transient species at 480 nm., for the temperatures shown.

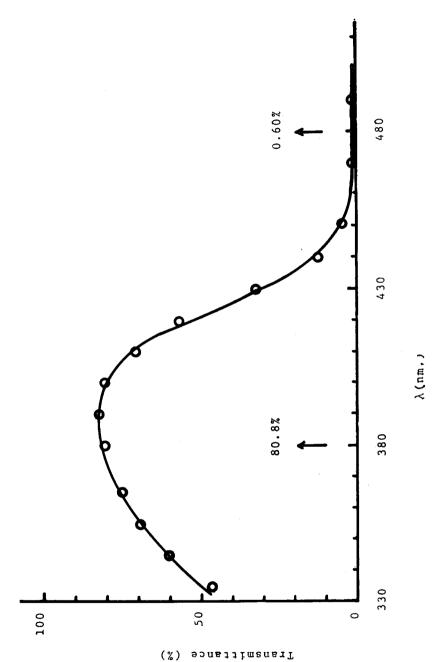


figure 2: The absorption of the filter solution.

0-methoxy and p-hydroxy derivatives. This interpretation of the effect of water is supported by the observation that the typical photochemical activity of salicylideneaniline is lost in equeous solutions. Anils of salicylaldehyde, in solid (8) or liquid (9) systems, are well known to undergo coloration, following ultra violet irradiation. By using flash techniques it is observed that the 480 nm., product of photochromism of salicylideneaniline in ethanol, gradually disappears upon increasing the water content of the solution. At 95 % H<sub>2</sub>O the photochemical process is totally suppressed. It is also established (8), that an OH group, ortho to the -CH = Nchain, is essential for photochromism and, from Infra Red and Xray data, that all orto -OH derivatives are intramolecularly hydrogen bonded (10). The effect of water on the photochemistry is thus a direct indication that the O-H...N bridge is destroyed in aqueous solutions. Either the photochemical or the spectroscopic effect of H,O, can thus be used to monitor the degree of intramolecular hydrogen bonding in the anil system. Data on the spontaneous fading (dark reaction) of the red state of a, -salicylideneaniline show good agreement with those of Cohen et al (4) this change approximates a first order reaction. The spontaneous fading of  $\alpha_2$ -salicylideneaniline is much slower than that of  $\alpha_1$ -salicylideneaniline.

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TABLE I.

TEMPERATURE 18.50 °C, DISPLACEMENT 54.0
I INFINITY 46.5 I INFINITY CORRECTED 100.5

TIME	ļ I	I+D	(I'+D) / (I+D)	A	LN (A)
0.0000, +0 1.0000, -4 2.0000, -4 3.0000, -4 4.0000, -4 5.0000, -4 6.0000, -4	1.4000, +1 1.5500, +1 1.7500, +1 1.9500, +1 2.0500, +1 2.2000, +1 2.3000, +1	6.8000, +1 6.9500, +1 7.1500, +1 7.3500, +1 7.4500, +1 7.6000, +1 7.700, +1	$\begin{array}{c} 1.4779, \ +0 \\ 1.4460, \ +0 \\ 1.4056, \ +0 \\ 1.3673, \ +0 \\ 1.3490, \ +0 \\ 1.3224, \ +0 \\ 1.3052, \ +0 \\ \end{array}$	3.9065, —1 3.6883, —1 3.4046, —1 3.1287, —1 2.9936, —1 2.7942, —1 2.6635, —1	$\begin{array}{c} -9.3994, \ -1 \\ -9.9742, \ -1 \\ -1.0775, \ +0 \\ -1.1620, \ +0 \\ -1.2061, \ +0 \\ -1.2750, \ +0 \\ -1.3229, \ +0 \\ \end{array}$

THE GRADIENT IS .... -6.5459, +2

THE INTERCEPT IS ..... -9.4374, -1

THE ERROR SOUARED IS .... 8.3822, —4

THE HALF LIFE (SECS) IS .... 1.0589, -3

THE INITIAL ABSORBENCE IS .... 3.9006, -1

# TEMPERATURE 19.20 °C, DISPLACEMENT 54.0 I INFINITY 57.5, I INFINITY CORRECTED 111.5

TIME	I	I+D	(I'+D) / (I+D)	A	LN (A)
0.0000, +0 2.0000, -4 4.0000, -4 6.0000, -4 8.0000, -4 1.0000, -3 1.2000, -3	3.4500, +1 3.9000, +1 4.2500, +1 4.5500, +1 4.8000, +1 5.0000, +1 5.1500, +1	$egin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} 1.2599, +0 \\ 1.1989, +1 \\ 1.1554, +0 \\ 1.1206, +0 \\ 1.0931, +0 \\ 1.0721, +0 \\ 1.0569, +0 \end{array}$	2.3102, —1 1.8143, —1 1.4448, —1 1.1387, —1 9.9052, —2 6.9634, —2 5.5314, —2	$\begin{array}{c} -1.4652, +0 \\ -1.7069, +0 \\ -1.9346, +0 \\ -2.1727, +0 \\ -2.4185, +0 \\ -2.6645, +0 \\ -2.8947, +0 \end{array}$

THE GRADIENT IS .... --1.1942, +3

THE INTERCEPT IS .... —1.4631, +0

THE ERROR SQUARED IS .... 1.6892, —4

THE HALF LIFE (SECS) IS .... 5.8042, -4

THE INITIAL ABSORBENCE IS .... 2.3104, -1

#### TEMPERATURE 23.50 °C DISPLACEMENT 54.0 I INFINITY 43.0, I INFINITY CORRECTED 97.0

TIME	I	I+D	(I'+D) / (I+D)	A	LN (A)
$\begin{bmatrix} 0.0000, & +0 \\ 2.0000, & -4 \\ 4.0000, & -4 \\ 6.0000, & -4 \end{bmatrix}$	1.8000, +1 2.3000, +1 2.7500, +1 3.1500, +1	7.2000, +1 $7.7000, +1$ $8.1500, +1$ $8.5500, +1$	1.3472, +0 1.2597, +0 1.1902, +0 1.1345, +0	2.9804, —1 2.3091, —1 1.7411, —1 1.2619, —1	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$
8.0000, —4 1.0000, —3 1.2000, —3	3.4000, +1 $3.6000, +1$ $3.8000, +1$	8.8000, +1 $9.0000, +1$ $9.2000, +1$	$ \begin{vmatrix} 1.1343, & +0 \\ 1.1023, & +0 \\ 1.0778, & +0 \\ 1.0543, & +0 \end{vmatrix} $	9.7374, —2 7.4901, —2 5.2922, —2	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

THE GRADIENT IS .... -1.4318, +3

THE INTERCEPT IS .... -1.1915, +0

THE ERROR SQUARED IS .... 3.0657, --3

THE HALF LIFE (SECS) IS .... 4.8411, —4

THE INITIAL ABSORBENCE IS .... 3.0083, -1

## TEMPERATURE 27.00 °C, DISPLACEMENT 54.0 I INFINITY 46,0, I INFINITY CORRECTED 100.0

TIME	I	I+D	(I'+D) / (I+D)	A	LN (A)
0.0000, —0 2.0000, —4 4.0000, —4 6.0000, —4 8.0000, —4	2.4500, +1 3.0500, +1 3.4500, +1 3.8000, +1 4.0500, +1	7.8500, +1 8.4500, +1 8.8500, +1 9.2000, +1 9.4500, +1	1.2739, +0 1.1834, +0 1.1299, +0 1.0870, +0 1.0582, +0	$\begin{array}{c} 2.4207, \; -1 \\ 1.6842, \; -1 \\ 1.2217, \; -1 \\ 8.3382, \; -2 \\ 5.6570, \; -2 \end{array}$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$
1.0000, —3 1.2000, —3	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} 9.6000, +1 \\ 9.7000, +1 \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	4.0822, —2 3.0459, —2	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

THE GRADIENT IS .... -1.7541, +3

THE INTERCEPT IS .... -1.4259, +0

THE ERROR SQUARED IS .... 4.5018, —3

THE HALF LIFE (SECS) IS .... 3.9516, —4

THE INITIAL ABSORBENCE IS .... 2.4193, —1

## TEMPERATURE 31.70 °C, DISPLACEMENT 54.0, I INFINITY 45.5, I INFINITY CORRECTED 99.5

TIME	I	I+D	(I'+D) / (I+D)	A	LN (A)
0.0000, +0	2.8000, +1	8.2000, +1	1.2134, +0	1.9344, —1	-1.6428, +0
$egin{array}{ccccc} 1.0000, & -4 \ 2.0000, & -4 \end{array}$	$egin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} 8.5500, +1 \\ 9.8500, +1 \end{array}$	$egin{array}{cccccccccccccccccccccccccccccccccccc$	1.5164, -1 $1.1716, -1$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
3.0000, -4 $4.0000, -4$	$egin{array}{cccccccccccccccccccccccccccccccccccc$	$egin{array}{cccccccccccccccccccccccccccccccccccc$	$egin{array}{cccccccccccccccccccccccccccccccccccc$	9.4808, -2 $7.2949, -2$	$\begin{bmatrix} -2.3559, +0 \\ -2.6180, +0 \end{bmatrix}$
5.0000, —4 6.0000, —4	4.0500, +1 $4.1500, +1$	9.4500, +1 $9.5500, +1$	1.0529, +0 $1.0419, +0$	5.1558, -2 $4.1031, -2$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

THE GRADIENT IS .... -2.6012, +3

THE INTERCEPT IS .... -1.6205, +0

THE ERROR SQARED IS .... 6.4904, --3

THE HALF LIFE (SECS) IS .... 2.6648, —4

THE INITIAL ABSORBENCE IS .... 1.9448, —1

## TEMPERATURE 36.30 °C, DISPLACEMENT 54.0 I INFINITY 61.0, I INFINITY CORRECTED 115.0

TIME	I	I+D	(I'+D) / (I+D)	A	IN (A)
0.0000, +0 1.0000, -4 2.0000, -4 3.0000, -4 4.0000, -4 5.0000, -4 6.0000, -4	$\begin{array}{c} 2.7000, \ +1 \\ 3.4000, \ +1 \\ 3.8500, \ +1 \\ 4.3000, \ +1 \\ 4.6000, \ +1 \\ 4.8500, \ +1 \\ 5.0500, \ +1 \end{array}$	$\begin{array}{c} 8.1000, \ +1 \\ 8.8000, \ +1 \\ 9.2500, \ +1 \\ 9.7000, \ +1 \\ 1.0000, \ +2 \\ 1.0250, \ +2 \\ 1.0450, \ +2 \\ \end{array}$	$\begin{array}{c} 1.4198, \ +0 \\ 1.3068, \ +0 \\ 1.2432, \ +0 \\ 1.1856, \ +0 \\ 1.1500, \ +2 \\ 1.1220, \ +0 \\ 1.1005, \ +0 \\ \end{array}$	3.5048, —1 2.6760, —1 2.1772, —1 1.7022, —1 1.3976, —1 1.1507, —1 9.5745, —2	$\begin{array}{c} -1.0484, +0 \\ -1.3183, +0 \\ -1.5245, +0 \\ -1.7707, +0 \\ -1.9678, +0 \\ -2.1622, +0 \\ -2.3461, +0 \end{array}$

THE GRADINET IS .... -2.1514, +3

THE INTERCEPT IS .... -1.0886, +0

THE ERROR SQUARED IS .... 4.6643, —3.

THE HALF LIFE (SECS) IS .... 3. 2218, —4

THE INITIAL ABSORBENCE IS .... 3.4396,—1

# TEMPERATURE 39.40 °C, DISPLACEMENT 54.0 I INFINITY 44.0, I INFINITY CORRECTED 98.0

TIME	I	I+D	(I'+D) / (I+D)	A	LN (A)
0.0000, +0 1.0000, -4 2.0000, -4 3.0000, -4 4.0000, -4 5.0000, -4 6.0000, -4	$egin{array}{cccccccccccccccccccccccccccccccccccc$	7.2000, +1 $7.8000, +1$ $8.2000, +1$ $8.6000, +1$ $8.8500, +1$ $9.1000, +1$ $9.2500, +1$	$\begin{array}{c} 1.3611, \ +0 \\ 1.2544, \ +0 \\ 1.1951, \ +0 \\ 1.1395, \ +0 \\ 1.1073, \ +0 \\ 1.0769, \ +0 \\ 1.0595, \ +0 \end{array}$	3.0830, —1 2.2826, —1 1.7825, —1 1.3062, —1 1.0196, —1 7.4108, —2 5.7759, —2	$\begin{array}{c} -1.1767, +0 \\ -1.4773, +0 \\ -1.7246, +0 \\ -2.0355, +0 \\ -2.2931, +0 \\ -2.6022, +0 \\ -2.8515, +0 \end{array}$

THE GRADIENT IS .... —2. 7975, +3

THE INTERCERT IS .... -1.1823, +0

THE ERROR SQUARED IS .... 1.6194, —3

THE HALF LIFE (SECS) IS .... 2.4778, —4

THE INITIAL ABSORBENCE IS ... 3.0694,—1

# TEMPERATURE 41.20 °C, DISPLACEMENT 54.0 I INFINITY 41.5, I INFINITY CORRECTED 95.5

TIME	I	I+D	(I'+D) / (I+D)	A	LN (A)
0.0000, +0 5.0000, -5 1.0000, -4 1.5000, -4 2.0000, -4 2.5000, -4 3.0000, -4	$\begin{array}{c} 2.3000, \ +1 \\ 2.6000, \ +1 \\ 2.8500, \ +1 \\ 3.1000, \ +1 \\ 3.2500, \ +1 \\ 3.4000, \ +1 \\ 3.5500, \ +1 \\ \end{array}$	7.7000, +1 $8.0000, +1$ $8.2500, +1$ $8.5000, +1$ $8.6500, +1$ $8.8000, +1$ $8.9500, +1$	$egin{array}{cccccccccccccccccccccccccccccccccccc$	2.1532, —1 1.7710, —1 1.4633, —1 1.1647, —1 9.8982, —2 8.1789, —2 6.4888, —2	$\begin{array}{c} -1.5356, +0 \\ -1.7310, +0 \\ -1.9219, +0 \\ -2.1501, +0 \\ -2.3128, +0 \\ -2.5036, +0 \\ -2.7351, +0 \end{array}$

THE GRADIENT IS .... -3.9532, +3 THE INTERCEPT IS....-1.5342, +0

THE ERROR SQUARED IS .... 1.3069. —3

THE HALF LIFE (SECS) IS .... 1.7534, -4

THE INITIAL ABSORBENCE IS .... 2.1548, —1

# TEMPERATURE 46.80 °C, DISPLACEMENET 54.0 I INFINITY 51.0, I INFINITY CORRECTED 105.0

TIME	I	I+D	(I'+D) / (I+D)	A	LN (A)
0.0000, —0 1.0000, —4 2.0000, —4 3.0000, —4 4.0000, —4 5.0000, —4 6.0000, —4	$egin{array}{cccccccccccccccccccccccccccccccccccc$	7.1000, +1 $8.1000, +1$ $8.8500, +1$ $9.3500, +1$ $9.7000, +1$ $1.0000, +2$ $1.0100, +2$	$\begin{array}{c} 1.4789, \ +0 \\ 1.2963, \ +0 \\ 1.1864, \ +0 \\ 1.1230, \ +0 \\ 1.0825, \ +0 \\ 1.0500, \ +0 \\ 1.0396, \ +0 \\ \end{array}$	3.9128, —1 2.5951, —1 1.7096, —1 1.1600, —1 7.9249, —2 4.8790, —2 3.8840, —2	$\begin{array}{c} -9.3833, \ -1 \\ -1.3490, \ +0 \\ -1.7663, \ +0 \\ -2.1542, \ +0 \\ -2.5352, \ +0 \\ -3.0202, \ +0 \\ -3.2483, \ +0 \end{array}$

THE GRADIENT IS .... -3.9433, +3

THE INTERCEPT IS .... —9.6150, —1

THE ERROR SQUARED IS .... 1.4803,—2

THE HALF LIFE (SECS) IS .... 1.7578, —4

THE INITIAL ABSORBENCE IS .... 3.9029, —1

# TEMPERATURE 53.00 °C, DISPLACEMENT 54.0 I INFINITY 55.0, I INFINITY CORRECTED 109.0

TIME	l I	I+D	(I'+D) / (I+D)	A	LN (A)
0.0000, +0 5.0000, -5 1.0000, -4 1.5000, -4 2.0000, -4 2.5000, -4 3.0000, -4	3.7000, +1 4.1500, +1 4.4500, +1 4.7500, +1 4.9500, +1 5.1000, +1 5.2000, +1	$\begin{array}{c} 9.1000, \ +1 \\ 9.5500, \ +1 \\ 9.8500, \ +1 \\ 1.0150, \ +2 \\ 1.0350, \ +2 \\ 1.0500, \ +2 \\ 1.0600, \ +2 \\ \end{array}$	$\begin{array}{c} 1.1978, \ +0 \\ 1.1414, \ +0 \\ 1.1066, \ +0 \\ 1.0739, \ +0 \\ 1.0531, \ +0 \\ 1.0381, \ +0 \\ 1.0283, \ +0 \\ \end{array}$	$\begin{array}{c} 1.8049, \1 \\ 1.3222, \1 \\ 1.0129, \1 \\ 7.1289, \2 \\ 5.1776, \2 \\ 3.7388, \2 \\ 2.7909, \2 \\ \end{array}$	$\begin{array}{c} -1.7121, +0 \\ -2.0233, +0 \\ -2.2898, +0 \\ -2.6410, +0 \\ -2.9608, +0 \\ -3.2864, +0 \\ -3.5788, +0 \end{array}$

THE GRADIENT IS .... -6.2839, +3

THE INTERCEPT IS .... -1. 6991, +0

THE ERROR SQUARED IS .... 2.0140, -3

THE HALF LIFE (SECS) IS .... 1.1030, —4

THE INITIAL ABSORBENCE IS .... 1.8111, —I

TEMPERATURE 55.00 °C, DISPLACEMENT 54.0 I INFINITY 51.0, I INFINITY CORRECTED 105.0

TIME	I	I+D	(I'+D) / (I+D)	A	LN (A)
0.0000, +0 2.5000, -5 5.0000, -5 7.5000, -5 1.0000, -4	$egin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} 8.4000, \ +1 \\ 8.6500, \ +1 \\ 8.9500, \ +1 \\ 9.2000, \ +1 \\ 9.4000, \ +1 \end{array}$	1.2500, +0 1.2139, +0 1.1732, +0 1.1413, +0 1.1170, +0	2.2314, —1 1.9382, —1 1.5972, —1 1.3217, —1 1.1067, —1	$ \begin{array}{c} -1.4999, +0 \\ -2.6408, +0 \\ -1.8343, +0 \\ -2.0237, +0 \\ -2.2012, +0 \end{array} $
$\begin{array}{c} 1.2500, -4 \\ 1.5000, -4 \end{array}$	$ \begin{bmatrix} 4.2000, +1 \\ 4.3500, +1 \end{bmatrix} $	$ \begin{vmatrix} 9.6000, & +1 \\ 9.7500, & +1 \end{vmatrix} $	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

THE GRADIENT IS .... -7.4523, +3

THE INTERCEPT IS .... -1.4717, +0

THE ERROR SQUARED IS .... 1.7290, —3

THE HALF LIFE (SECS) IS .... 9.3011, -5

THE INITIAL ABSORBENCE IS .... 2.2715, —1

TABLE II

LEAST SQUARE FIT (THERMODYNAMIC)

T (C)	T (K)	1/T	K	LN (K)
18.5	291.7	3.4282, —3	6.5459, +2	6.4840, +0
19.2	292.4	3.4200, —3	1.1942, +3	7.0852, +0
23.5	296.7	3.3704, —3	1.4318, +3	7.2667, +0
27.0	300.2	3.3311, —3	1.7541. +3	7.4697, +0
31.7	304.9	3.2798, —3	2.6012, +3	7.8637. +0
36.3	309.5	3.2310, —3	2.1514, +3	7.6739, +0
39.4	312.6	3.1990, —3	2.7975, +3	7.9365, +0
41.2	314.4	3.1807, —3	3.9532, +3	8.2823, +0
46.8	320.0	3.1250, —3	3.9433, —3	8.2798. +0
53.0	226.2	3.0656, -3	6.2839, +3	8.7457, +0
55.0	328.2	3.0569, —3	7.4523, +3	8.9163, +0

THE GRADIENT IS .... 5.2157, +3

THE INTERCEIT IS .... 2.4735, +1

THE ERROR SQUARED IS .... 3.5699, —1

THE ACTIVATION ENERGY IS....1.0364, +4

THE ENTROPY CHANGE IS....-1.1404, +1

#### REFERENCES

- [1] G. H. Brown and W. G. Shaw, Rev. Pure Apply, Chem. 11-2- (1961).
- [2] M. D. Cohen, Y. Hirshberg and G. M. J. Schmidt. "Hydrogen bonding" Pergamon press Inc., N. Y. (1959).
- [ 3 ] N. Ebara, Nippon Kogaku Zasshi 82-941- (1961).
- [4] M. D. Cohen, G. M. J. Schmidth, S. Flavian, J. Chem. Soc. 1964-2041 (1964).
- [ 5] J. D. Margerum and J. A. Sousa, Appl. Spectry. 19, 91 (1965).
- [ 6] G. C. Pimental and A. L. McClellan, The Hydrogen Bond (W. H. Freeman and co.,)
- [7] G. C. Pimental, J. Am. Chem. Soc. 79, 3323 (1957).
- [8] M. D. Cohen, Y. Hirshberg, and G. M. J. Schmidt, J. Chem. Soc. 1964, 2051.
- [ 9] D. G. Anderson and G. Wettermark, J. Am. Chem. Soc. 87, 1433 (1965).
- [10] (a) S. B. Hendricks, O. K. Wulf, G. E. Hilbert and U. Liddel. J.Am. Chem. Soc. 58, 1991 (1936).
  - (b) J. Bregman, L. Leiserowitz, and G. M. J. Schmidt, J. Chem. Soc. 1964-2068.
  - (c) J. Bregman, L. Leiserowitz, and K. Osaki, ibid. 1964, 2086.

#### ÖZET

Salicylidene Aniline'nin yakın mor üstü ışınlarla bombardımanı ile sarı olan rengi kırmızıya dönüşmekte ve kırmızı hal çok çabuk eski haline dönmektedir, bu renk değişimi görünür bölgedeki ışınlarla hızlandırılabilir. 18.5 ve 55°C sıcaklıkları arasında renkli izomerin reaksiyonları incelenmiş ve uyarma enerjileri ile entropi değişimi hesaplanmıştır. (α₁) tipinde renk değişimi hızlı olduğu için ışıkesimi (flash photolysis) tekniği kullanılmıştır.

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