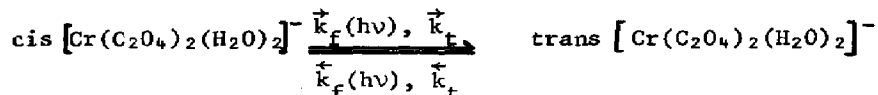# PHOTOISOMERIZATION OF K$\left[Cr(C_2O_4)_2(H_2O)_2\right]$ IN AQUEOUS SOLUTION

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This paper deals with the photoisomerization kinetics of K$\left[Cr(C_2O_4)_2(H_2O)_2\right]$ in aqueous solution which has not been yet investigated. The irradiation was carried out at $\lambda = 405$, 436, 546 and 578 nm by using a conventional photochemical setup. The sample was maintained at 25 $^{\circ}$C and the absorbance measurements were done at $\lambda = 417$ nm in the irradiation cell.

The system investigated consisted of

$$\text{cis} \left[Cr(C_2O_4)_2(H_2O)_2\right]^- \overset{\vec{k}_f(h\nu),\ \vec{k}_t}{\underset{\overset{\leftarrow}{k}_f(h\nu),\ \overset{\leftarrow}{k}_t}{\rightleftharpoons}} \text{trans} \left[Cr(C_2O_4)_2(H_2O)_2\right]^-$$

where $\vec{k}_f, \overset{\leftarrow}{k}_f$ and $\vec{k}_t, \overset{\leftarrow}{k}_t$ are the rate constants of the forward and back photoisomerization reactions and thermal reactions, respectively.

We used a kinetic treatment similar to that proposed by Adamson[1] and we obtained the following equation :

$$-\log \frac{A - A_{\infty}}{A_o - A_{\infty}} = \frac{\vec{k}_f + \overset{\leftarrow}{k}_f + \vec{k}_t + \overset{\leftarrow}{k}_t}{2.303}\ t + C \tag{1}$$

where A_o, A, A_{∞} are the absorbances of the cis isomer at zero time, at a given time t and in the photostationarity state, respectively. Under photostationarity conditions the following relationship can be derived:

$$K_f = \frac{\vec{k}_f + \vec{k}_t}{\overset{\leftarrow}{k}_f + \overset{\leftarrow}{k}_t} = \frac{\alpha^{\infty}\text{trans}}{1 - \alpha^{\infty}\text{trans}} = \text{const.} \tag{2}$$

α^{∞} trans being the trans isomer percentage.

Our experimental data verified first order kinetics for the photoisomerization reaction as well as for the thermal reaction at all wavelengths investigated. Under these conditions the quantum yields of both isomers are given by

$$\phi_{cis} = \frac{\vec{k}_f}{\varepsilon_{cis}\, f(A)\ell Q_0} \qquad\qquad \phi_{trans} = \frac{\overleftarrow{k}_f}{\varepsilon_{trans}\, f(A)\ell Q_0} \qquad\qquad (3)$$

where ε_{cis} and ε_{trans} are the absorption coefficients of these isomers (M min^{-1}), ℓ is the optical depth of the system (cm), $f(A)$ is an absorbance function of the sample which we maintained constant during the irradiation and Q_0 is the incident radiation intensity (M min^{-1}).

Our experimental data obtained on irradiation in both absorption bands of the complex are summarized in Table 1. Our experiments give evidence of the photochromic character of this isomerization.

TABLE 1

λ (nm)	$f(A)Q_0 \times 10^2$ (M min^{-1})	K_f	$k_s \times 10^2$ (min^{-1})	$\vec{k}_f \times 10^2$ (min^{-1})	$\overleftarrow{k}_f \times 10^2$ (min^{-1})	$\phi_{cis} \times 10^2$	$\phi_{trans} \times 10^2$
578	6.47	0.372	5.23	1.28	1.10	0.13	0.37
578	6.59	0.372	5.32	1.31	1.17	0.13	0.39
546	2.12	0.341	5.27	1.20	1.22	0.39	0.98
546	2.19	0.387	5.18	1.31	1.03	0.41	0.80
436	1.05	0.264	3.31	0.555	0.992	0.31	2.13
436	1.58	0.232	5.18	0.839	1.500	0.306	2.13
405	0.606	0.222	4.10	0.608	0.645	0.51	1.77

where $k_s = \vec{k}_f + \overleftarrow{k}_f + \vec{k}_t + \overleftarrow{k}_t$

In order to prove the existence of a back photochemical trans→cis process which we assumed in our kinetic treatment we compared the rate of trans→cis isomerization under irradiation and in its absence and we observed an evident photo-acceleration of the thermal reaction (Fig. 1).

Concerning the photoisomerization mechanism we incline to the view proposed by Kelm and Harris[2] for the thermal isomerization of $K[Cr(C_2O_4)_2(H_2O)_2]$, although our results are not sufficient to decide it. Our opinions rely on the fact that we used a radiation energy (50-70 kcal mol^{-1}) which is much higher than that of the activation energy of the corresponding thermal process (20 kcal mol^{-1}). It is generally known that the excited states of the complexes can present a geometry that is modified in comparison with that of the ground state[3]. This favours the isomerization[4,5]. Under our conditions it is very likely that excited states are involved, the geometry of which is modified in such a way that ring opening and closing of the complex is permitted and that therefore their photoisomerization is possible.
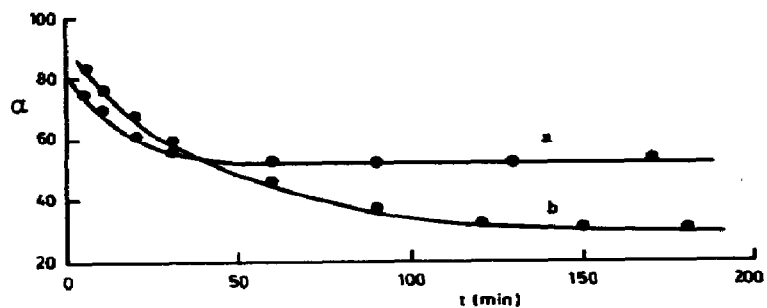
Fig. 1. Photo–acceleration of trans→cis isomerization: (a) on irradiation, (b) without irradiation.

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