

A FLASH PHOTOLYSIS INVESTIGATION OF PHOTOCHROMIC TRIPHENYLFORMAZAN

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(Received July 18, 1980; in revised form December 19, 1980)

Summary

Triphenylformazan does not exhibit photochemical conversion of the red *cis-syn* form into the yellow *cis-anti* isomer nor does this reaction proceed thermally as reported previously. The yellow *trans-anti* isomer is formed thermally from the *cis-syn* form without intermediate formation of the yellow *cis-anti* isomer. A modified reaction scheme is presented.

1. Introduction

Based on irradiation experiments and absorption spectroscopic measurements in the temperature range 116 - 293 K we have recently modified [1] the cyclic isomerization scheme originally proposed by Kuhn and coworkers [2, 3]. Using Kuhn's assignment of the isomers of triphenylformazan (TPF) to the spectroscopically observable species, we were able to show that only the *trans-cis* isomerizations of the azo group proceed photochemically, that the reverse reactions proceed both photochemically and thermally and that photoinduced isomerizations about the C=N double bond could be excluded. However, no unequivocal proof for the thermal conversion of B into C could be given (for the designation of the TPF isomers see Fig. 2) since at low temperatures the degree of conversion α ($A \rightarrow B$) is very small in the photo-stationary state and the reaction $C \rightarrow D$ may also be induced by radiation of wavelength 546 nm. Flash photolysis experiments were intended to clarify this question and to refine and supplement the hitherto known results.

2. Experimental

All solutions of TPF in thoroughly purified toluene (5×10^{-6} M) were prepared immediately before flashing under exclusion of actinic light. Since the presence of oxygen had not been found to influence the photochemical behaviour of TPF the solutions were not degassed. Unless otherwise stated all solutions were flashed only once. A cut-off filter ($\lambda > 450$ nm, Schott

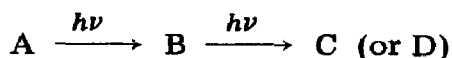
GG5) was inserted between the flash lamps and the sample. The intensity of the analysing light beam was reduced by interference and neutral density filters until no photoreactions due to the measuring light were detectable. The transmission changes after the photolysis were measured and were analysed at 405 and 546 nm.

The most essential features of the flash photolysis apparatus used are briefly described elsewhere [4]. The extreme sensitivity of the kinetic parameters of the TPF solutions to the smallest traces of acid or alkaline impurities demands the greatest care in the preparation and handling of the solutions to obtain reproducible results.

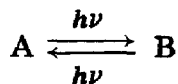
3. Results and discussion

3.1. Mechanism of formation of form D

At 405 nm there is no change in transmission immediately after the flash. At this wavelength the following relation is fulfilled for the molar absorptivities of the forms A, B, C and D: $\epsilon_A \approx \epsilon_B \ll \epsilon_C < \epsilon_D$ [1]. This confirms the previous result [1] that there is no photoisomerization of A or B to form C or D. If a consecutive photoreaction



occurs then there should exist a range in which the absorbance due to the concentration of C (or D) formed per flash depends quadratically on the flash intensity [5]. Gradual reduction of the flash intensity over one order of magnitude did not reveal such a dependence. The flash intensity used in all further experiments was so high that the transmission changes measured were practically independent of it. This is easily explained by the establishment of the photostationary state



All kinetic curves are first order within experimental accuracy. As an example, Table 1 shows the rate constants evaluated in one series of measurements at the wavelengths indicated. Surprisingly, the rate constants evaluated for the absorbance build-up at 405 nm exceed those measured previously [1] for the reaction $C \rightarrow D$ by approximately one order of magnitude (e.g. $k(26^\circ\text{C}) = 0.1 \text{ s}^{-1}$, $E_A = 67 \text{ kJ mol}^{-1}$). However, if the *trans-syn* form A is increasingly converted into the *trans-anti* form D by repeated flashing, then on flash photolysis a biexponential increase in the absorbance at 405 nm is observed initially and it becomes singly exponential after practically complete conversion. The rate constants evaluated under these conditions fit well into the previously determined Arrhenius plot for the reaction $C \rightarrow D$.

It follows unequivocally from these facts that C is not involved as an intermediate in the conversion of B into D. Since at 546 nm $\epsilon_C \approx \epsilon_D \approx 0$

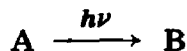
TABLE 1

Measured rate constants for the absorbance build-up at 405 and 546 nm and ratios of remaining and initial absorbance differences

T (K)	k_{405} (s^{-1})	k_{546} (s^{-1})	$\Delta E_{\infty}/\Delta E_0$
288.6	0.29	0.21	0.67
299.1	0.43	0.56	0.45
309.1	1.3	1.2	0.25
329.7	5.1	4.8	0.08
339.7	11.3	12.1	0.13
349.6	—	24.2	0.05

The errors in the rate constants result mainly from errors in defining the end point of the reactions. They amount to about $\pm 10\%$ for a single measurement.

and $\epsilon_A > \epsilon_B$, immediately after the flash a decrease in the original absorbance due to the conversion



is observed at this wavelength. After the initial depletion the absorbance again increases, because of the thermal reverse reaction $B \rightarrow A$, but does not attain the value before the flash because of the competitive conversion $B \rightarrow D$. The lifetime of D is of the order of hours if highly purified hydrocarbons are used as solvents; consequently the reaction $D \rightarrow A$ was neglected in this study. Within the experimental accuracy the rate constants evaluated at 405 and 546 nm are equal. The ratios of the persisting absorbance differences to those immediately after the flash (both with respect to the absorbance before flashing) are given in Table 1, column 4. They show that the proportion of molecules B reacting back to A increases appreciably with increasing temperature; the reaction $B \rightarrow D$ becomes almost negligible at the highest temperature employed.

All these results are consistent with the following simple reaction scheme involving only two thermal reactions:



3.2. Determination of rate constants

From the known solutions of the corresponding set of differential equations [6] we may derive the following expression for the ratio $\Delta E_{\infty}/\Delta E_0$ using $\Delta E_0/d = (\epsilon_A - \epsilon_B)[B]_0$ and $t \rightarrow \infty$ (d is the cell thickness and $[B]_0$ is the initial concentration of B):

$$\frac{\Delta E_{\infty}}{\Delta E_0} = \frac{1}{\epsilon_A - \epsilon_B} \frac{k_2}{k_1 + k_2} (\epsilon_A - \epsilon_D)$$

This expression allows the evaluation of the directly immeasurable individual rate constants k_1 and k_2 from $k_{405} = k_{546} = k_1 + k_2$. The results are shown in Fig. 1. Since at the highest temperatures employed the value of ΔE_{∞} becomes

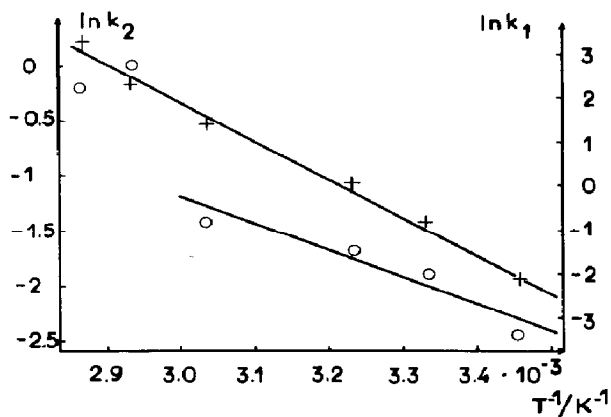
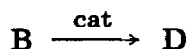


Fig. 1. An Arrhenius plot for the individual rate constants k_1 (+, right-hand ordinate) and k_2 (o, left-hand ordinate).

increasingly erroneous (finally in excess of 100%), the values of k_2 for the temperatures 66.5 and 76.5 °C were not included in the regression line; however, their inclusion would not change the result qualitatively. It is remarkable that in repeated series of measurements the constants k_1 were found to be well reproducible; the previously mentioned sensitivity to traces of acid or alkaline impurities affects only the reproducibility of the k_2 values. The use of the extinction coefficients determined at much lower temperatures ($\epsilon_A^{546} = 16\,000 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $\epsilon_B^{546} = 6200 \text{ l mol}^{-1} \text{ cm}^{-1}$ [1]) in the calculation of k_1 and k_2 may introduce an additional systematic error. Therefore we regard the parameters $E_A = 19 \pm 4 \text{ kJ mol}^{-1}$ and $\log_{10} A = 2.5 \pm 1$, which were obtained from the Arrhenius plot for k_2 , as semiquantitative estimates only. Irrespective of its considerable experimental error the exceptional low order of magnitude of the pre-exponential factor A requires some discussion.

3.3. Catalytic role of species A

Because the conversion $B \rightarrow D$ requires isomerization about two double bonds a highly improbable transition state can be conceived. This is specially true for a catalysed reaction



To determine whether one of the involved species A, B or D itself may catalyse the reaction $B \rightarrow D$, the kinetics of the formation of D at 405 nm were analysed by varying the analytical TPF concentration in the range $2 \times 10^{-6} - 5 \times 10^{-5} \text{ M}$. The results clearly exclude both a higher order in B and an autocatalysis by D. The kinetic analysis is consistent with the assumption of catalysis by A. Linear regression of the observed first-order rate constants

according to

$$k_{405}^{obs} = k_{405} + k'_{405}[A]$$

(10 measurements at 25 °C) yields $k_{405} = 0.8 \pm 0.5 \text{ s}^{-1}$ and $k'_{405} = (6.2 \pm 1.8) \times 10^4 \text{ s}^{-1}$. Up to $2 \times 10^{-5} \text{ M}$ TPF the concentration dependence of the rate constants lies within the experimental error.

The parameters $E_A = 70.2 \pm 1.7 \text{ kJ mol}^{-1}$ and $\log_{10}A = 11.9 \pm 0.3$, which were evaluated from the Arrhenius plot for k_1 , are in complete agreement with the expectations for *cis-trans* isomerization about the N=N bond.

3.4. Conclusions

The results of this investigation may be interpreted by including previously reported results [1] and using the scheme given in Fig. 2.

The thermodynamically stable form of TPF ($\lambda_{max} = 495 \text{ nm}$) is converted by a photochemical *trans-cis* isomerization about the N=N double bond into the isomer B which is also red and shows a lower absorption intensity. The reason for the comparatively long-wavelength absorption of B might be a torsion about the C-N single bond; this torsion could possibly result in a better conjugation in the azohydrazone moiety of the molecule through the formation of a weak five-membered cyclic hydrogen-bridge interaction. According to Avramenko and Stepanov [7] the longest wavelength absorption band is the result of a $\pi\pi^*$ transition in the azohydrazone moiety of the molecule.

Form B may revert photochemically as well as thermally to the original form. A competitive reaction forming the *trans-anti* isomer D occurs at room temperature with a comparable rate constant. The isomer C, with a *cis-anti* configuration, is only formed photochemically from D. C is also yellow and has a smaller molar absorptivity than does D. The reverse reaction $C \rightarrow D$ proceeds both photochemically and thermally.

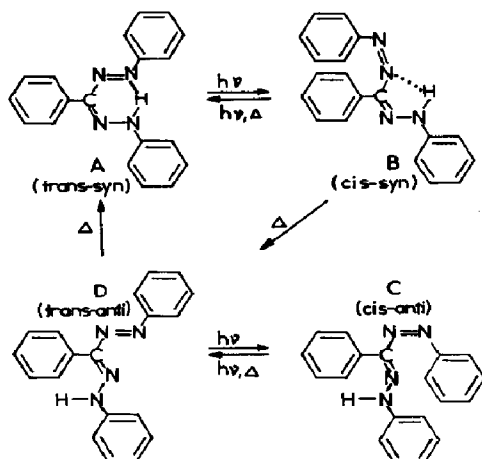


Fig. 2. The reaction scheme proposed for TPF.

Acknowledgment

The authors are deeply indebted to Professor Dr. R. Paetzold for stimulating discussions.

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