Competition between tunnel- and viscosity-effects on bimolecular hydrogen-transfer reaction

Uwe Kensy, Karl-Heinz Grellmann* and Manuel Mosquera González

Max-Planck-Institut für Biophysikalische Chemie, D-3400 Göttingen, Germany
1) Permanent address: Universidad de Santiago, Santiago de Compostela, Spain

Abstract

The photocyclization of a methylsubstituted diphenylamine results in the formation of a transient zwitterionic dihydrocarbazole. The transient converts into a stable dihydrocarbazole by an intramolecular, sigmatropic hydrogen shift and by an intermolecular hydrogen exchange reaction. The rates of both reactions are governed by hydrogen tunnel effects. The intermolecular hydrogen exchange is the first example for a bimolecular reaction where tunnel effects have been observed. The role of solvent viscosity is discussed.

INTRODUCTION

In recent years a number of intramolecular hydrogen transfer reactions in the singlet ground state as well as in excited triplet states have been investigated where quantum mechanical tunnel effects clearly determine the rates of the transfer reaction (ref. 1). To our knowledge, no such tunnel effects have been observed so far on an intermolecular hydrogen transfer reaction. In this paper we wish to describe a photoreaction which initiates an intramolecular hydrogen transfer as well as an intermolecular hydrogen exchange reaction.

RESULTS AND DISCUSSION

The diphenylamine derivative A photocyclizes adiabatically in its triplet state (ref. 2), \( ^3A^* \), yielding the zwitterionic intermediate \( ^3Z^* \) which subsequently relaxes to its singlet ground state \( ^1Z \).

Depending on temperature, the photocyclization \( ^3A^* \rightarrow ^3Z^* \) takes place within \( ~10 \text{ ns at } 300 \text{ K} \)
and $\sim 100 \mu$s at 100 K; the intersystem crossing process $3^Z \rightarrow 1^Z$ is temperature independent (rate constant $k_{isc} = 3 \times 10^6 \text{s}^{-1}$). The lifetime of $1^Z$ is at all temperatures several orders of magnitude longer than that of its precursors. Therefore, if one analyses the decay of $1^Z$, which has an absorption maximum at $\lambda_{max} = 520 \text{ nm}$, its formation can be taken to be instantaneous.

Three reaction channels are responsible for the decay of $1^Z$ (cf. Scheme 1): 1. Thermally activated ring-opening back to the starting material (rate constant $k_d$). 2. Rearrangement by an intramolecular sigmatropic [1,8]-hydrogen-shift (rate constant $k_{hs}$) yielding as final product the stable dihydrocarbazole $D$. 3. Intermolecular hydrogen exchange (overall rate constant $\theta_{ex}$) yielding the same endproduct $D$ as the intramolecular process $k_{hs}$.

The ring-opening reaction has a high activation energy ($k_b = 5 \times 10^{12} \exp(-\Delta E_b/RT)$; $\Delta E_b = 57 \text{ kJ/mol}$). It prevails at temperatures above $\sim 200 \text{ K}$ and therefore, the decay of $1^Z$ is within experimental error monoexponential in that temperature region. At temperatures below $\sim 180 \text{ K}$ the rates of the intramolecular rearrangement ($k_{hs}$) and the bimolecular exchange reaction ($\theta_{ex}$) dominate and the decay of $1^Z$ is of mixed first- and second-order.

At $T = 173 \text{ K}$, solutions of the amines $A_H$ and $A_D$ in nitrogen-purged 3-methylpentane (3MP) were photolysed in mg-amounts (ref. 3). The resulting photoproducts were carefully analysed by NMR-spectroscopy. According to this analysis only one photoproduct (detection limit $\geq 5\%$) was formed, namely the dihydrocarbazole $D$. After the photolysis of the deuterated compound $A_D$ one $D$-atom was found on the diene-ring of $D$, the other 2 remained at the aromatic ring. Since at 173 K both, the first- and the second-order reaction contribute substantially to the decay of $1^Z$, we conclude that the two decay processes yield the same photoproduct $D$. 

**Scheme 1**

\[
1^Z + 1^Z \xrightarrow{k_d} (1^Z \cdots 1^Z) \xrightarrow{k_{ex}} 2 \cdot 1^D
\]

\[\theta_{ex} = k_{ex} / (k_d + k_{ex})\]

\[k_d \sim k\text{, } k_{ex}\]

**Scheme 2**
In this paper we discuss the second-order reaction in more detail. We propose that the zwiterion $\text{Z}^\pm$ forms an encounter complex ($\text{Z}^\pm-\text{Z}^\pm$) which either dissociates ($k_{-d}$) or forms two molecules of $\text{Z}^\pm$ by a mutual hydrogen exchange (rate constant $k_{ex}$, cf. Scheme 2). The overall second-order rate constant of this reaction is

$$\theta_{ex} = \frac{k_d \cdot k_{ex}}{k_{ex} + k_{-d}}$$

If $k_{ex} < k_{-d}$, the process becomes reaction controlled, i.e., $\theta_{ex} \approx k_d \cdot k_{ex} / k_{-d}$, and if $k_{ex} > k_{-d}$, the process becomes diffusion controlled, i.e., $\theta_{ex} \approx k_d$.

We determined $\theta_{ex}$ in the temperature range 74 K to 180 K in the two nonpolar solvents 3MP and the mixture cyclopentane/isopentane, 1:4 by volume (CI). The result is shown as Arrhenius plot in Fig. 1. For both solvents accurate viscosity data are available (ref. 4). Included in Fig. 1 are the diffusion rate constants $k_d$(MP) and $k_d$(CI) which were calculated using the corresponding viscosity data $\eta$(MP) and $\eta$(CI) and assuming $k_d = 8 \frac{RT}{3\eta}$.

Obviously, above $\sim 100$ K the exchange reaction is in both solvents reaction controlled, because the calculated diffusion rate constants $k_d$(MP) and $k_d$(CI) are 2 to 5 orders of magnitude larger than $\theta_{ex}$. In 3MP, which is at lower temperatures much more viscous than the mixture CI, the Arrhenius plot of $\theta_{ex}$(MP) bends down steeply below $\sim 90$ K and the extrapolation of the $k_d$(MP) -values (dashed line in Fig. 1) clearly shows that in 3MP around 90 K the exchange rate constant
For the light amine $A_H$, the exchange reaction becomes diffusion controlled. Accordingly, in the less viscous solvent CI this effect is observed at a much lower temperature (~77 K). Moreover, between 80 K and 100 K the overall rate constant $\theta_{ex}^H$ becomes temperature independent. The latter observation strongly indicates that in CI at least in this horizontal part of the Arrhenius plot the rate of the exchange reaction is solely determined by tunnel effects. The isotope effect which one observes if the exchanging hydrogen atoms are replaced by deuterium ($\theta_{ex}^D$ in Fig. 1) corroborates this conclusion. In the diffusion controlled region (below 90 K in 3MP and below 75 K in CI) the isotope effect should vanish because it is very unlikely that $k_d$ is sensitive to isotopic substitution. Unfortunately, for technical reasons it was impossible to extend the measurements with $A_D$ to temperatures below ~100 K (cf. Fig. 1). Decay rates with half-lifes of several days had to be determined and 3MP as well as CI tend to crystallize if kept for several days at low temperatures. For the same reason we could not perform measurements with hydrocarbon solvents which had a higher viscosity than 3MP.

**CONCLUSION**

The diphenylamine derivative $A$ is a compound where tunnel effects on a light-initiated bimolecular hydrogen transfer reaction could be observed for the first time. The requirements for detecting such effects are rather stringent: Intramolecular first-order processes have to be slow enough to make competing second-order processes observable. Furthermore, the temperature dependence of the solvent viscosity has to be such that the transfer process is still reaction controlled at low temperatures. The comparison of the rate data in the two solvents employed demonstrates how important it is to meet this requirement (cf. Fig. 1). We feel that the temperature-independence of the reaction rates in CI between 80 K and 100 K can only be explained in terms of quantum mechanical tunnel effects. The observed isotope effects strongly indicate that above 100 K thermally activated hydrogen tunneling determines the exchange rates, too.

**REFERENCES**