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

Uwe Kensy, Karl-Heinz Grellmann* and Manuel Mosquera González[1]

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 *intra*molecular hydrogen transfer reactions in the singlet ground state as well as in excited triplet states have been investigated where quantum mechanical tunnel

$R = CH_3$

A   Z   D

L = H: A_H Z_H
L = D: A_D Z_D
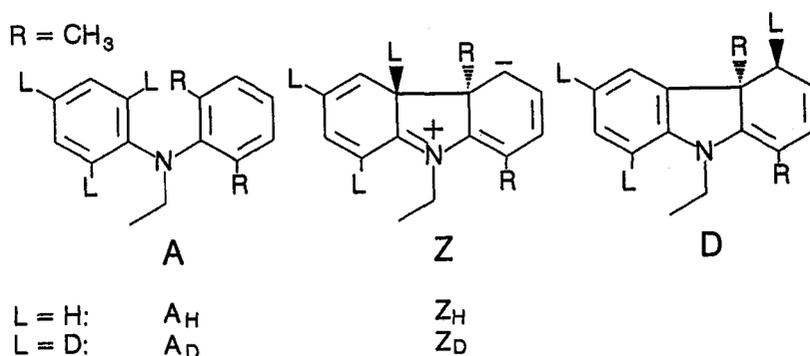
effects clearly determine the rates of the transfer reaction (ref. 1). To our knowledge, no such tunnel effects have been observed so far on an *inter*molecular hydrogen transfer reaction. In this paper we wish to describe a photoreaction which initiates an intramolecular hydrogen transfer as well as 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 ns at 300 K

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

Three reaction channels are responsible for the decay of ^1Z (cf. Scheme 1): 1. Thermally activated ring-opening back to the starting material (rate constant k_b). 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 θ_{ex}) yielding the same endproduct **D** as the intramolecular process k_{hs}.

Scheme 1

$$^1Z + {}^1Z \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} ({}^1Z \cdots {}^1Z) \xrightarrow{k_{ex}} 2\,{}^1D$$

$$\theta_{ex} = k_d \cdot k_{ex} / (k_{-d} + k_{ex})$$

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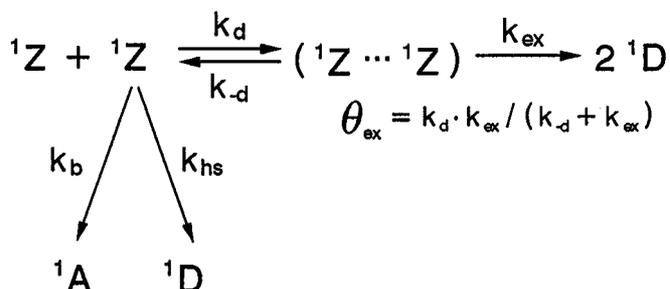
The ring-opening reaction has a high activation energy ($k_b = 5 \times 10^{12}$ exp($-\Delta E_b/RT$); $\Delta E_b = 57$ kJ/mol). It prevails at temperatures above ~ 200 K and therefore, the decay of ^1Z is within experimental error monoexponential in that temperature region. At temperatures below ~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

At T = 173 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 ≥ 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 ^1Z, we conclude that *the two decay processes yield the same photoproduct **D***.

Scheme 2
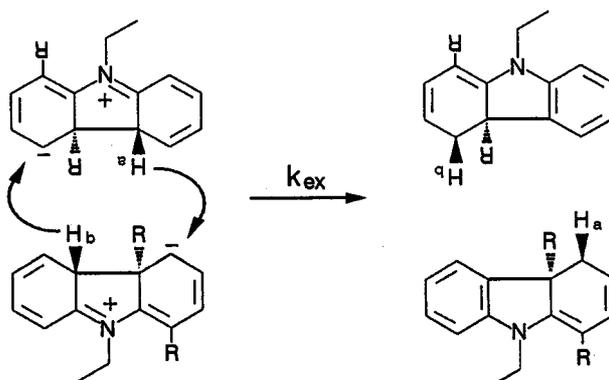
In this paper we discuss the second-order reaction in more detail. We propose that the zwitterion ^1Z forms an encounter complex ($^1Z\cdots^1Z$) (rate constant k_d) which either dissociates (k_{-d}) or forms two molecules of ^1D by a mutual hydrogen exchange (rate constant k_{ex}, cf. Scheme 2). The overall second-order rate constant of this reaction is

$$\theta_{ex} = k_d \cdot k_{ex} / (k_{ex} + k_{-d})$$

If $k_{ex} \ll k_{-d}$, the process becomes *reaction controlled*, i.e., $\theta_{ex} \approx k_d \cdot k_{ex}/k_{-d}$, and if $k_{ex} \gg k_{-d}$, the process becomes *diffusion controlled*, i.e., $\theta_{ex} \approx k_d$.
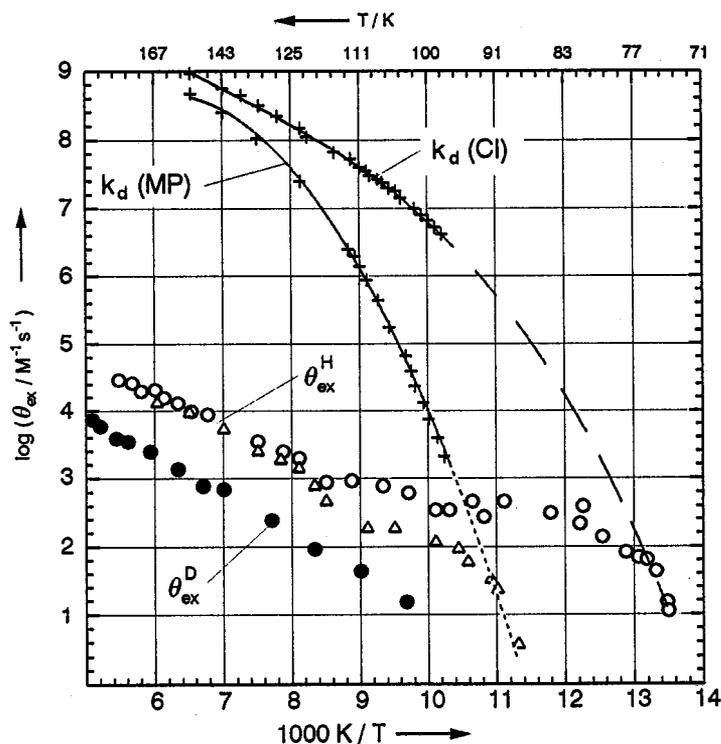
Figure 1: Arrhenius plot of experimentally determined second-order rate constants θ_{ex} in 3MP (triangles) and CI (dots and circles) and of diffusion rate constants calculated from viscosity data.

We determined θ_{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 η(MP) and η(CI) and assuming $k_d = 8\,RT/3\eta$.

Obviously, above ~ 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 θ_{ex}. In 3MP, which is at lower temperatures much more viscous than the mixture CI, the Arrhenius plot of θ_{ex}(MP) bends down steeply below ~ 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

θ^H_{ex} for the light amine A_H becomes diffusion controlled. Accordingly, in the less viscous solvent CI this bending is observed at a much lower temperature ($\sim$ 77 K). Moreover, between 80 K and 100 K the overall rate constant θ^H_{ex} 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 (θ^D_{ex} 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 extent the measurements with A_D to temperatures below $\sim$ 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

1. For a recent review, see V.A. Benderskii and V.I. Goldanskii,
   Intern. Rev. Phys. Chem. 11, 1 (1992)
2. K.H. Grellmann, U. Schmitt and H. Weller, Chem. Phys. Letters 88, 40 (1982)
3. K.H. Grellmann, U. Schmitt and H. Weller, J. Chem. Soc. Chem. Comm. 1982, 591
4. (a) H. Lesche, D. Klemp and B. Nickel, Z. Phys. Chem. 141, 239 (1984)
   (b) A.A. Ruth, B. Nickel and H. Lesche, Z. Phys. Chem. in the press (1992)