

MICROENVIRONMENTAL EFFECTS IN SOLID-STATE REACTIONS. DISPERSIVE KINETICS OF CONFORMATION-DEPENDENT CHARGE DELOCALIZATION IN ALIPHATIC DIAMINE RADICAL CATIONS

ANDRZEJ MARCINEK, JERZY GĘBICKI* AND ANDRZEJ PŁONKA*
Institute of Applied Radiation Chemistry, Technical University, 90-924 Łódź, Poland

The kinetics of conformation-dependent charge delocalization in radical cations generated from a series of α,ω -diaminoalkanes, $(\text{CH}_3)_2\text{N}(\text{CH}_2)_n\text{N}(\text{CH}_3)_2$, ($n = 1-3$) in a 3-methylpentane glassy solution at 90 K are discussed in terms of dispersive kinetics with the use of the time-dependent rate constant in the form $k(t) = Bt^{\alpha-1}$. It was found that the activation energy distribution function became broader as the number of methylene groups separating the two nitrogen atoms increased, and that this process was accompanied by a substantial increase in the mean value of the activation energy.

INTRODUCTION

Kinetic observations of chemical reactions in a non-fluid medium are often difficult to analyse by applying classical kinetic equations. Problems may arise from the perturbation caused by the solvent rigidity, as different molecules in a solid sample experience different microenvironments. This effect, in principle, can lead to the distribution of activation barriers and to complex (dispersive) kinetics. Recent approaches to dispersive kinetics in condensed media¹⁻³ offer various mathematical models for treating experimental data. Sponser *et al.*,³ applying a method called 'distribution slicing', showed experimentally that the rate dispersion may arise from a distribution of activation energies (E) with the Arrhenius pre-exponential factor (A) remaining constant.

Since elucidation of the matrix perturbation in solid-state reactions is highly challenging and only a few systems have been analysed so far, we decided to study the kinetic behaviour of unimolecular reactions of structurally designed molecules for which microenvironmental effects are expected to be a function of molecular structure. The chosen model reaction obeys conformation-dependent charge delocalization in radical cations generated from a series of α,ω -diaminoalkanes $(\text{CH}_3)_2\text{N}(\text{CH}_2)_n\text{N}(\text{CH}_3)_2$, ($n = 1-3$) in a 3-methylpentane glassy matrix.⁴

RESULTS AND DISCUSSION

The α,ω -diaminoalkanes studied were N,N,N',N' -tetramethyldiaminomethane ($n = 1$; **1**), N,N,N',N' -tetramethyldiaminoethane ($n = 2$; **2**) and N,N,N',N' -tetramethyldiaminopropane ($n = 3$; **3**). A mechanistic discussion of conformation-dependent charge delocalization in radical cations of **1**, **2** and **3** together with relevant results and descriptions of the experimental details were given previously.⁴ It was found that the time needed to achieve a suitable geometry for charge delocalization was a function of the number of methylene groups separating the nitrogen atoms. The most complex initial conformation is expected for **3** and it was not surprising that this molecule needs the longest time to achieve a suitable conformation for charge delocalization. In this case the through-space interactions are dominant and they are expected to be strong only if two nitrogen atoms are in close vicinity. Our recent work⁴ clearly supports the view that conformational motion restricted by the rigid matrix environment leads to substantial changes in the time-resolved absorption spectra, which in turn reflect intramolecular interactions in diamine radical cations. However, the discussion of the kinetics was left open and will be present here.

Intramolecular conformational changes lowering the energy of radical cations lead to structures suitable for charge delocalization. This intramolecular rearrangement should, in principle, follow first-order kinetics. However, the experimental data do not follow such

* Authors for correspondence

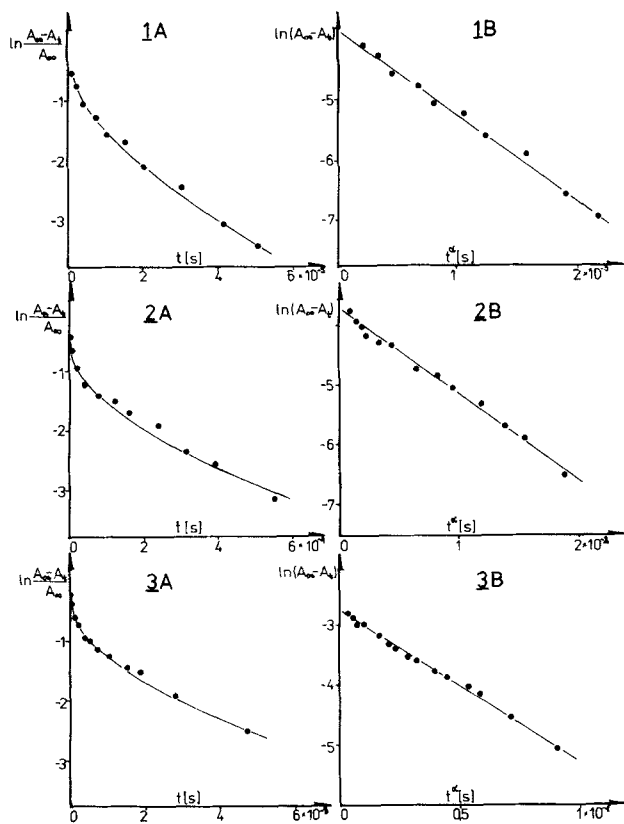


Figure 1. Experimental data for the formation of diamine radical cations in pulse-irradiated 3-methylpentane glass at 90 K presented in coordinates suitable for (A) classical and (B) dispersive kinetics. Wavelength monitored: 1 and 2, 750 nm; 3, 500 nm (cf. Ref. 4)

kinetics, as is shown in Figure 1 (curves 1A, 2A and 3A). The kinetics are more complex, suggesting a distribution of the initial conformation leading to distribution of the reaction rates. Therefore, we have analysed our results in terms of dispersive kinetics using the time-dependent rate coefficient in the form

$$k(t) = Bt^{\alpha-1} \quad (1)$$

where the coefficient $0 < \alpha \leq 1$ measures the reactivity dispersion.^{1,2} The first-order kinetic equation

$$-dc/dt = k(t)c \quad (2)$$

with the time-dependent rate coefficient [equation (1)] on integration gives the relation

$$\ln(c/c_0) = -(B/\alpha)t^\alpha = -(t/\tau_0)^\alpha \quad (3)$$

which fits the experimental results well (Figure 1, curves 1B, 2B and 3B).

Phenomenologically, the decrease in the rate coeffi-

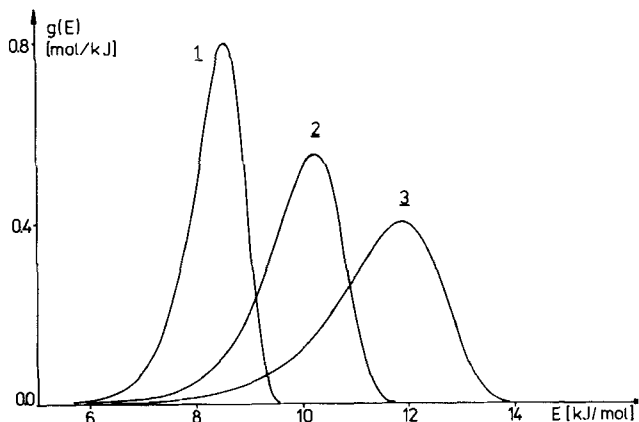


Figure 2. Densities of activation energy distribution for the formation of diamine radical cations

cient $k(t)$ with time according to equation (1) implies² that the activation energy for reaction increases as

$$E = E_0 + (1 - \alpha)RT[\ln(t/\tau_0)] \quad (4)$$

where $\tau_0 = (\alpha/B)^{1/\alpha}$ for the first-order reaction. This enables one to obtain the distribution function for activation energy $F(E)$ from $F(t) = 1 - (c/c_0)$. The densities of the activation energy distribution function,

$$g(E) = dF(E)/dE \quad (5)$$

are depicted in Figure 2 for a value of the pre-exponential factor in the Arrhenius equation equal to $\log A = 10$. The first moments of the activation energy distribution,² i.e. the mean value of activation energy $\langle E \rangle$

$$\langle E \rangle = E_0 - [0.577(1 - \alpha)RT/\alpha] \quad (6)$$

and the dispersion characterizing the width of the activation energy distributions,

$$\sigma^2 = \pi^2/6[(1 - \alpha)RT/\alpha]^2 \quad (7)$$

are given in Table 1 together with the kinetic parameters used for data fitting. It is clearly seen that the activation energy distribution function becomes broader as the number of methylene groups separating the two nitrogen atoms increases. This effect is accompanied by a substantial increase in the raising

Table 1. Rate and activation parameters for the formation of diamine radical cations with delocalized charge

Diamine	α	τ_0 (s)	$\langle E \rangle$ (kJ mol ⁻¹)	σ^2 (kJ ² mol ⁻²)
1	0.62	9.1×10^{-6}	8.3	0.34
2	0.53	8.8×10^{-5}	9.9	0.72
3	0.45	8.1×10^{-4}	11.4	1.37

time of the absorption characterizing the radical cation with delocalized charge.

One can intuitively visualize this observation in the following way. The conformational flexibility of a diamine is greater for molecules having a longer chain separating the two nitrogen atoms. Greater conformational flexibility causes greater conformational disorder of diamine molecules embedded in the glassy matrix. After ionization, the radical cation initially formed retains the structure of the neutral parent and conformational motion monitored as the absorption change with time leads to the structure of the lowest energy characterized by the greatest interactions. Greater initial conformational disorder should be characterized by a broader activation energy distribution function and a longer time should be needed to achieve a favourable conformation. It is expected that the molecule in the initial conformation surrounded by its own microenvironment possesses a characteristic activation barrier for conformational motion which is partially a function of this microenvironment.

All these expectations were verified by experimental

results presented above. The results discussed here were obtained in a 3-methylpentane glassy matrix, but similar conclusions can be drawn from the results obtained with methylcyclohexane glass. There is no doubt that a correlation exists between the kinetic behaviour of a conformationally driven reaction and the structure of the matrix site accommodating the reacting molecule.

ACKNOWLEDGEMENT

This work was supported by research programme CPBP 01.19

REFERENCES

1. A. Pfonka, *Time-Dependent Reactivity of Species in Condensed Media, Lecture Notes in Chemistry*, Vol. 40. Springer, Heidelberg (1986).
2. A. Pfonka, *Annu. Rep. Prog. Chem.* **85**, 47-75 (1989).
3. M. B. Sponsler, R. Jain, F. D. Coms and D. A. Dougherty, *J. Am. Chem. Soc.* **111**, 2240-2252 (1989).
4. J. Gębicki, A. Marcinek and C. Stradowski, *J. Phys. Org. Chem.* **3**, 606-610 (1990).