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Equilibria of the Formation of N^1-(9-Fluorenylidene)-ethylenediamine from Fluorenone and Ethylenediamine in Acetonitrile

Effect of Alkali Metal Cations

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The equilibrium of the formation of N^1-(9-fluorenylidene)-ethylenediamine from fluorenone and ethylenediamine has been studied in acetonitrile at 25 °C using a polarographic method. The equilibrium constant K for this reaction has been found to depend on the nature of supporting electrolyte cation; the reactivity increases with a decrease of the crystallographic cation radius. The enhanced reactivity is attributed to the hydration of a cation by H_2O molecules lost in the reaction. A plot of $\log K$ versus the free hydration enthalpy of a cation gives a fairly straight line.

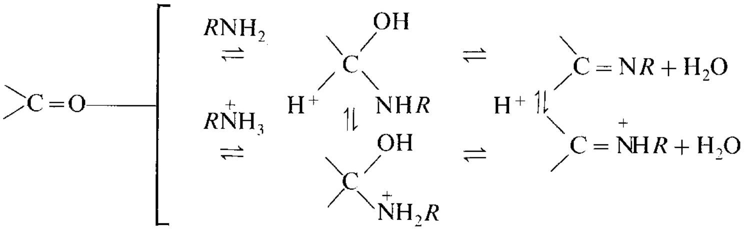
(Keywords: Imine formation; Cation effect; Ethylenediamine; Fluorenone; Polarography)

Bildungsgleichgewichte von N^1-(9-Fluorenyliden)-ethylendiamin aus Fluorenon und Ethylendiamin in Acetonitril. Der Effekt von Alkalimetall-Kationen

Das Gleichgewicht der Bildung von N^1-(9-Fluorenyliden)-ethylendiamin aus Fluorenon und Ethylendiamin in Acetonitril bei 25 °C wurde mittels einer polarographischen Methode untersucht. Es wurde festgestellt, daß die Gleichgewichtskonstante K dieser Reaktion von der Natur des Elektrolyt-Kations abhängt: die Reaktivität steigt mit abnehmendem kristallographischen Radius der Kationen an. Die erhöhte Reaktivität wird der Hydratation der Kationen mit Wassermolekülen, die bei der Reaktion freigesetzt werden, zugeschrieben. Die graphische Darstellung von $\log K$ gegen die freien Hydratationsenthalpien der Kationen ergibt eine Gerade von zureichender Korrelation.

Introduction

The formation of an imine is an important intermediate step in many reactions of aldehydes and ketones. This conversion, particularly interesting for polarographic determination of aliphatic carbonyl compounds, was initially studied by *Zuman* in the late fifties[1—3]. Then, growing interest in electrochemical properties of aldehydes and ketones and their imino derivatives led to numerous results in aqueous solutions which have been reviewed by *Turyan*[4]. The significant finding of these studies is the equilibrium scheme (1):


(1)

in which the intermediate (carbinolamine) is usually unstable and looses water to give an imino derivative. As follows from this scheme, the equilibria are influenced by hydrogen ion concentrations.

Ethylenediamine reacts also with ketones to give corresponding ketimines[5—8]. Obviously, the processes are *pH*-dependent; their kinetics have been described in Ref.[9]. We have found, moreover, that in non-aqueous media the equilibrium constant for the formation of N^1-(9-fluorenylidene)-ethylenediamine from fluorenone and ethylenediamine is also dependent on the nature of alkali metal cations. The purpose of the present report is to describe this problem in acetonitrile solutions. Experiments were performed using electrochemical techniques.

Experimental

Polarographic and cyclic voltammetric measurements were made in a three electrode system using a Radelkis OH-105 apparatus. For scan rates greater than $100\,mV\,s^{-1}$ an oscillopolarograph OP-3 (Poland) was used. The half-wave potentials are referred to an aqueous SCE. The dropping mercury electrode was characterized by drop time 2.0 s (a drop timer was used throughout the experiments); a hanging mercury drop electrode was constructed according to Ref.[10].

Acetonitrile was purified using a conventional method[11] and additionally dried with molecular sieves 3 Å-type. Ethylenediamine was refluxed over sodium and distilled under argon. Prior to use, the solvent was again refluxed over lithium and distilled under argon. The water content in the solvents, determined by gas chromatography, was about 10^{-3}%.

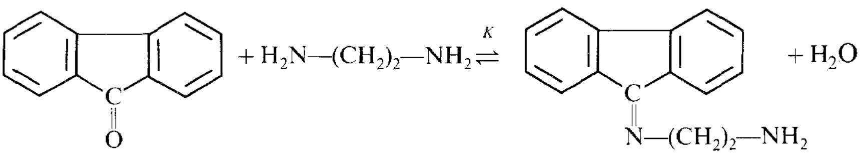
The electrolytes were perchlorates of AR grade which were dried in a vacuum dessicator over P_2O_5 at 60° (tetraethylammonium perchlorate) and 180° ($KClO_4$, $NaClO_4$ and $LiClO_4$), respectively. Fluorenone was purified by recrystallization from ethanol. Solutions in the electrochemical cell were purged of dissolved oxygen with oxygen free argon. Argon was presaturated by bubbling through the solvent. All measurements were performed at 25 ± 0.1 °C.

Results and Discussion

Polarographic and cyclic voltammetric curves of 1.0 mM fluorenone in acetonitrile containing 0.10 M $(C_2H_5)_4NClO_4$ as supporting electrolyte show two one-electron reversible waves with $E_{1/2}$-values —1.33 V and —1.76 V, respectively. Such a picture is characteristic for the electroreduction of aromatic ketones in rigorously aprotic conditions[12]. On the contrary, polarographic curves of fluorenone in ethylenediamine with 0.10 M tetraethylammonium perchlorate show only one diffusion controlled wave with $E_{1/2} = -1160$ mV. Coulometric experiments at a potential corresponding to the plateau of this wave were carried out to determine the number of electrons transferred in electroreduction. The number of faradays, n_{app}, consumed per mole of fluorenone was 1.95 ± 0.06. Cyclic voltammetric measurements indicated that the cathodic wave gives no anodic peak corresponding to the oxidation of the electroreduction product. Such a shape of the voltammogram was found to be independent of scan rate (from 0.05 to 10 V s^{-1}) and depolarizer concentration (from 0.08 to 4.2 mM).

The depolarizer in ethylenediamine solutions has been considered to be the corresponding imino derivative of fluorenone. To obtain additional evidence, we have synthesized this compound, according to the known procedure for fluorenone imine[13]. The results of elementary analysis of the product were fairly consistent with N^1-(9-fluorenylidene)-ethylenediamine (found C 80.88 H 6.52 N 12.25, calculated C 81.05 H 6.65 N 12.60). Moreover, this compound showed two one-electron cathodic waves in N,N-dimethylformamide solutions, 0.1 M $(nC_4H_9)_4NClO_4$, separated by some 580 mV, similarly as reported earlier for fluorenone imine[14].

Taking into account these observations we have considered the equilibrium



(2)

To gain further insight into the problem, the effect of an addition of varying ammounts of ethylenediamine to the acetonitrile solution of 1.0 mM fluorenone was examined. The polarograms registered in the presence of 0.10 M $(C_2H_5)_4NClO_4$ are presented in Fig. 1.

Curve A reproduces the first polarographic wave of fluorenone in the absence of ethylenediamine. After an addition of this species the new

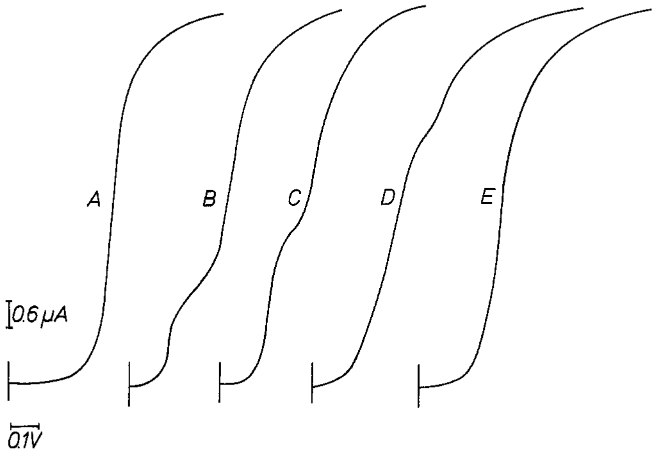


Fig. 1. Polarographic curves (first reduction step) of 1.0 mM fluorenone in acetonitrile—ethylenediamine mixed solvents. Concentration of ethylenediamine: A 0.00 M, B 0.20 M, C 0.45 M, D 0.90 M, and E 1.50 M. Supporting electrolyte: 0.10 M $(C_2H_5)_4NClO_4$. Starting potential: —1.00 V

Table 1. *Effect of supporting electrolyte cations on the equilibrium constant K for the formation of* N^1*-(9-fluorenylidene)-ethylenediamine in acetonitrile*

Supporting electrolyte, 0.10 M	Concentration of ethylenediamine, M		$K \times 10^4$
$(C_2H_5)_4NClO_4$	0.10		0.5
	0.20		0.5
	0.30		0.6
	0.40		0.5
	0.45		0.7
	0.90		0.6
		mean value	0.57
$KClO_4$	0.07		1.8
	0.10		1.4
	0.15		1.6
		mean value	1.6
$NaClO_4$	0.10		2.3
	0.20		2.0
	0.30		2.2
	0.45		2.5
	0.70		2.5
		mean value	2.3
$LiClO_4$	0.10		6.0
	0.30		6.4
	0.45		5.8
	0.60		6.0
	1.50		5.8
		mean value	6.0

reduction wave (pre-wave) is formed at more positive potentials (curve B). The height of this pre-wave increase with an increase of ethylenediamine concentration (curves B—E). As a consequence, only one cathodic wave is registered in solutions containing above 2 *M* of ethylenediamine.

Quite similar pictures may be observed when $KClO_4$, $NaClO_4$ and $LiClO_4$ are used as supporting electrolytes. The significant result of these investigations is the effect of cations on the equilibrium constant *K*. Taking into account that the waves of fluorenone and N^1-(9-fluorenylidene)-ethylenediamine are diffusion controlled, we have calculated *K*-values from polarographic curves. The results are collected in Table 1.

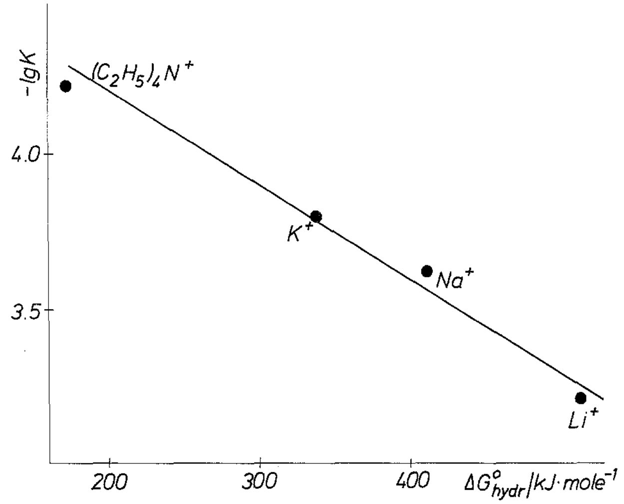


Fig. 2. Plot of the logarithm of the equilibrium constant for the formation of N^1-(9-fluorenylidene)-ethylenediamine vs. the free hydration enthalpies of cations

As can be seen from this table, the equilibrium constant for the formation of N^1-(9-fluorenylidene)-ethylenediamine from fluorenone and ethylenediamine depends on the nature of a cation. The data indicate that *K* decreases with an increase of crystallographic cation radius. What is, however, the possible explanation of this phenomenon?

It has been mentioned that H_2O molecules are lost in reaction (2). Consequently, we assume that the cation hydration is the important contributor to the equilibrium constant *K*. The reason can be that log *K* is a simple function of ΔG°_{hydr} (Fig. 2); here ΔG°_{hydr} stands for the free hydration enthalpy of a cation[15, 16]. That is, the stronger the cation hydration, the more favoured becomes the formation of N^1-(9-fluorenylidene)-ethylenediamine.

The formation of imines was known to be subject to *Brønsted* acid catalysis at least in aqueous solutions. Our results demonstrate that in aprotic conditions these processes may also be influenced by *Lewis* acids. Since this phenomenon is interesting for organic polarography, investigations will be continued.

Acknowledgement

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References

[1] *Zuman P.*, Collection Czechoslov. Chem. Communs **15**, 839 (1950).

[2] *Zuman P.*, Chem. Listy **45**, 65 (1951).

[3] *Zuman P.*, Topics in Organic Polarography. New York: Plenum. 1970.

[4] *Turyan Ya. I.*, Khimitcheskie Reaktsii v Polarografii, Chapt. 3.2.2. Moskva: Khimia. 1980.

[5] *Hall M. Y.*, Anal. Chem. **31**, 2007 (1959).

[6] *Hine J.*, *Holod M. S.*, *Chess W. K., Jr.*, J. Amer. Chem. Soc. **95**, 4270 (1973).

[7] *Hine J.*, *Li W. S.*, J. Org. Chem. **40**, 2622 (1975).

[8] *Hine J.*, *Li W. S.*, *Ziegler J.*, J. Amer. Chem. Soc. **102**, 4403 (1980).

[9] *Hine J.*, *Chou Y.*, J. Org. Chem. **46**, 649 (1981).

[10] *Kemula W.*, *Kublik Z.*, Anal. Chim. Acta **18**, 104 (1958).

[11] *Mann C. K.*, Electroanalytical Chemistry (*Bard A. J.*, ed.), Vol. 3, p. 57. New York: Marcel Dekker. 1969.

[12] *Jensen B. S.*, *Parker V. D.*, J. Chem. Soc. Chem. Commun. **1974**, 367.

[13] *Arcus C. L.*, *Mesley R. J.*, J. Chem. Soc. **1953**, 178.

[14] *Barnes J. H.*, *Triebe F. M.*, *Hawley M. D.*, J. Electroanal. Chem. **139**, 395 (1982).

[15] *Abraham M. H.*, *Liszi J.*, J. Chem. Soc. Faraday Trans. I **74**, 1604, 2858 (1978).

[16] *Abraham M. H.*, *Liszi J.*, J. Inorg. Nucl. Chem. **43**, 143 (1981).