

## Thermokinetic study on the inactivation reactions of 1-methylphthalazinium ylids

MARIA CAPROȘU\*, LUCIA ODOCHIAN\*, ȘT. DIMA\*\*, M. DUMITRAȘ\* and MAGDA  
PETROVANU\*

\*The "Al. I. Cuza" University, Faculty of Chemistry, Bd. Copou 11, Iasi 6600, Romania and

\*\*The "Dunarea de Jos" University, Galati, Romania

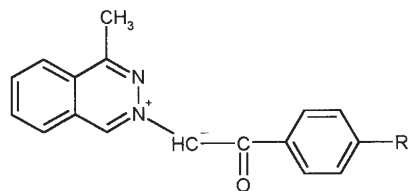
(Received 11 October 2002, revised 9 January 2003)

**Abstract:** The present paper consists in a thermokinetic study on the dimerization reactions of 1-methylphthalazinium ylids with  $-\text{NO}_2$  (ylid 1) and, respectively,  $-\text{O}-\text{CH}_3$  (ylid 2) substituents in the *p* position of the benzoyl radical bound to the ylidic carbanion. From experimental data, the reaction order and rate constants have been calculated. The reaction order  $n = 2$  confirmed the ylids' dimerization reactions, while the values of the rate constants,  $k_2 = 3.093 \times 10^{-2} \text{ L/mol s}$  and, respectively,  $2.16 \times 10^{-1} \text{ L/mol s}$  for the dimerization of ylids 1 and 2 made evident the higher reactivity of ylid 2 *versus* ylid 1. The same conclusion is also supported by the results of the thermodynamic study based on the chemical affinity of the two reactions, when  $A^{\circ}_{\text{dim},1} < A^{\circ}_{\text{dim},2}$ .

**Keywords:** 1-methylphthalazinium ylids, dimerization, inactivation, thermokinetics (reaction order, rate constants, chemical affinity).

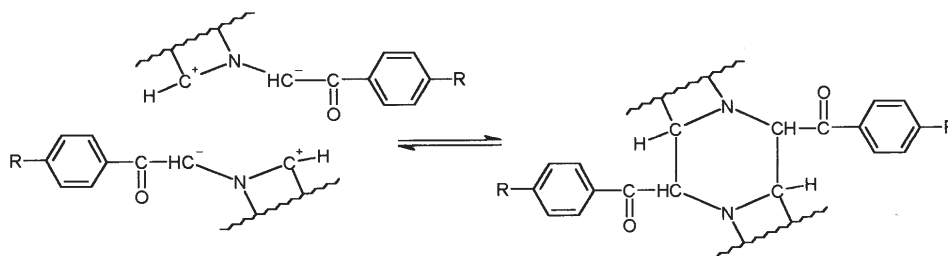
### INTRODUCTION

In previous studies, devoted to the synthesis and reactivity of cycloimmonium ylids,<sup>1</sup> Petrovanu *et al.* showed that one of the most important factors influencing the stability of cycloimmonium ylids is the nature of the substituents bound to the ylidic carbanion.<sup>2,3</sup> Delocalization of the ylidic carbanion's negative charge is favored by the presence of the groups with electron-withdrawing effect (such as the  $-\text{NO}_2$  group in the *p* position of the benzoyl radical – ylid 1), resulting in structure stabilization. In the



case of electron-repelling groups (such as  $-\text{O}-\text{CH}_3$  group in the *p* position of the benzoyl radical – ylid 2), structure destabilization occurs.

Also, the inactivation of these ylids has been evidenced to occur by a dimerization process based on a 3+3 dipolar cycloaddition.<sup>4</sup>



Aiming at confirming the above results on ylids' reactivity, a thermokinetic study on their inactivation through dimerization has been developed. As far as we know, another similar approach has not been mentioned in literature.

The kinetic study aimed at evaluating the reaction orders and the rate constants<sup>5-7</sup> from experimental data by applying three different methods<sup>8,9</sup>: differential, integral and, respectively, the half-life time method, by computer processing the experimental kinetic curves. The results obtained were found to be in good agreement.

The conclusions of the thermodynamic study, based on the values of the reaction enthalpies for the two inactivation processes, obtained by means of the standard formation enthalpies of the participants, theoretically calculated on mechanoquantum bases (the MNDO method<sup>10</sup>), supported the conclusions of the kinetic study.

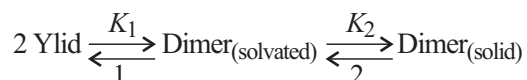
#### EXPERIMENTAL

The dimerization reactions of the two ylids were followed in methanol, at its boiling temperature (64 °C), under reflux. Ylids' concentration at various moments was determined by pH-metric titration<sup>5,6</sup> with a  $10^{-2}$  M methanolic solution of  $\text{HClO}_4$ , on employing a M.P. 220 Mettler-Toledo type potentiometric pH-meter, using a glass electrode, the pH values at the equivalence point being known from a previous paper.<sup>11</sup>

#### RESULTS AND DISCUSSION

Figures 1 (a and b) and 2 (a and b) plot the kinetic curves of ylids 1 and 2.

For a kinetic interpretation it has been taken into account that the very low solubility of the obtained dimers – experimentally stated by their solid-phase separation as early as the initial stages of the reaction – significantly shifts the equilibrium towards their formation:



The elementary equilibria, denoted 1 and 2, are characterized by the equilibrium constants:

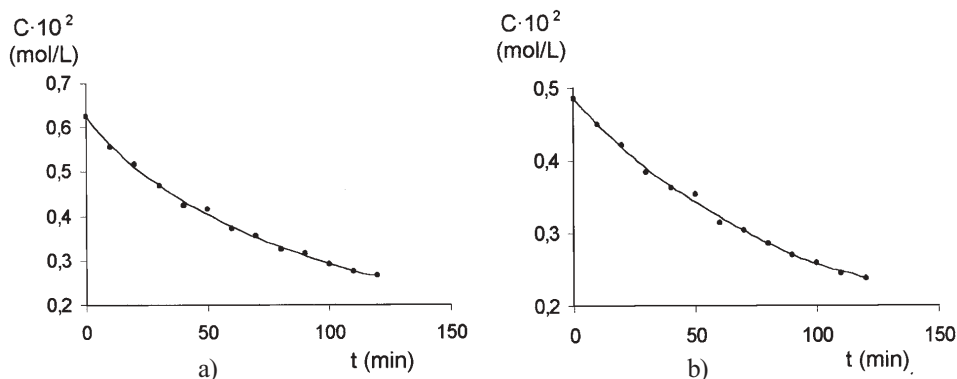


Fig. 1. Kinetic curves of ylid 1 in the dimerization reaction: (a) –  $c_{01} = 6.25 \times 10^{-3}$  mol/L;  
(b) –  $c_{02} = 4.85 \times 10^{-3}$  mol/L.

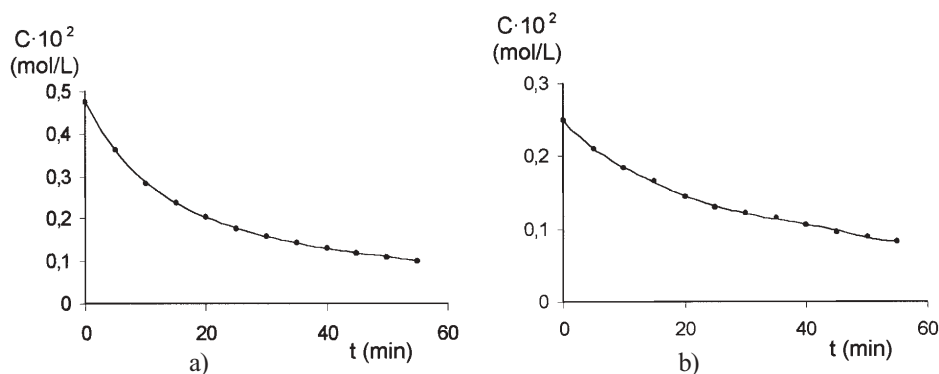


Fig. 2. Kinetic curves of ylid 2 in the dimerization reaction: (a) –  $c_{01} = 4.8 \times 10^{-3}$  mol/L;  
(b) –  $c_{02} = 2.5 \times 10^{-3}$  mol/L.

$$K_1 = \frac{[\text{Dimer}_{(\text{solvated})}]}{[\text{Ylid}]}; K_2 = \frac{a_{\text{solid}}}{[\text{Dimer}_{(\text{solvated})}]} = \frac{1}{S_0} \quad (1)$$

where  $S_0$  is the dimer's intrinsic solubility, and  $a_{\text{solid}}$  the activity of the solid dimer.

The equilibrium constant of the global process is given by:

$$K = \frac{[a_{\text{solid}}]}{[\text{Ylid}]^2} = K_1 \cdot K_2 = \frac{K_1}{S_0} \quad (2)$$

As a conclusion, the existence of the heterophasic equilibrium 2 with a very high equilibrium constant determines the global process to evolve far from equilibrium, which permits modeling (from the kinetic point of view) of the global process of dimerization as a simple, unilateral reaction.<sup>12</sup>

For the determination of the kinetic parameters by the differential method, the fundamental kinetic equation was used in a logarithmic form:

$$\ln v = \ln k + n \ln c \quad (3)$$

where  $v = d[\text{Ylid}]/dt$  and  $c = [\text{Ylid}]$

Obtaining of the  $v = f(c)$  dependence involved interpolation of the  $c = f(t)$  experimental data by using cspline function included in Mathcad 5.0 Plus and numeric derivation of the obtained interpolation function. Figures 3 and 4 plot the  $\ln v = f(\ln c)$  dependencies for the inactivation of ylids 1 and 2, respectively.

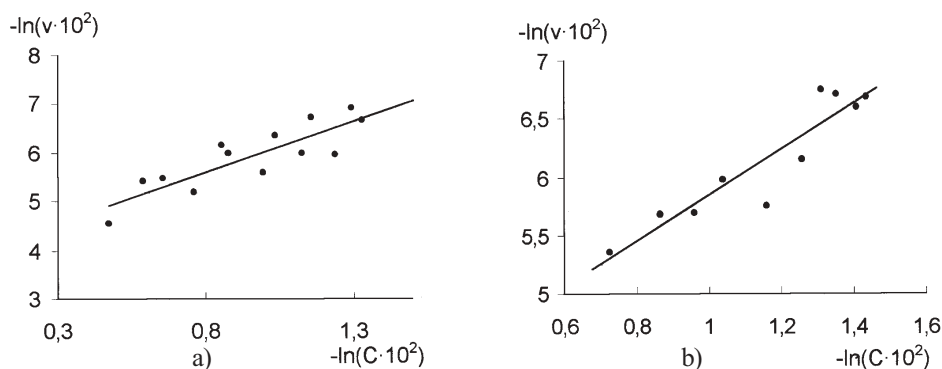


Fig. 3. The  $\ln v = f(\ln c)$  dependence for the dimerization reaction of ylid 1: (a) –  $c_{01} = 6.25 \times 10^{-3}$  mol/L; (b) –  $c_{02} = 4.85 \times 10^{-3}$  mol/L.

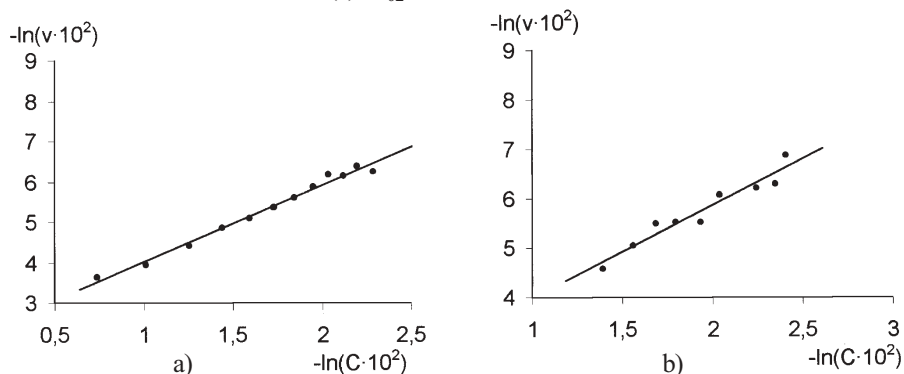


Fig. 4. The  $\ln v = f(\ln c)$  dependence for the dimerization reaction of ylid 2: (a) –  $c_{01} = 4.8 \times 10^{-3}$  mol/L; (b) –  $c_{02} = 2.5 \times 10^{-3}$  mol/L.

Table I lists the reaction orders and rate constants obtained by this method

TABLE I. Reaction orders and rate constants obtained by the differential method for the dimerization reactions of the two ylids

	Ylid 1		Ylid 2	
	$c_{01} = 6.25 \times 10^{-3}$ mol/L	$c_{02} = 4.85 \times 10^{-3}$ mol/L	$c_{01} = 4.80 \times 10^{-3}$ mol/L	$c_{02} = 2.50 \times 10^{-3}$ mol/L
$n$	2.072	1.9598	1.8995	1.9003
$k/(L/mol \text{ s})$	0.03174	0.03414	0.1999	0.210

while Table II gives the correlation coefficients obtained by substitution of the experimental data in the linearized integral kinetic equations corresponding to different reaction orders.

TABLE II. Correlation coefficients for various reaction orders

<i>n</i>	Kinetic equation	$R^2$ (Ylid 1)		$R^2$ (Ylid 2)	
		$c_{01} = 6.25 \times 10^{-3}$ mol/L	$c_{02} = 4.85 \times 10^{-3}$ mol/L	$c_{01} = 4.80 \times 10^{-3}$ mol/L	$c_{02} = 2.50 \times 10^{-3}$ mol/L
0	$c_0 - c = kt$	0.8206	0.9022	0.0201	0.6346
0.5	$c_0^{1/2} - c^{1/2} = \frac{1}{2} kt$	0.9102	0.9498	0.5473	0.8225
1	$\ln(c_0 - c) = kt$	0.9647	0.9792	0.8337	0.9331
1.5	$c^{-1/2} - c_0^{-1/2} = \frac{1}{2} kt$	0.9911	0.9912	0.9648	0.9855
2	$c^{-1} - c_0^{-1} = kt$	0.9956	0.9965	0.9997	0.9958
2.5	$c^{-5/2} - c_0^{-5/2} = \frac{3}{2} kt$	0.9839	0.9856	0.9804	0.9776

Analysis of the above data leads to the conclusion that the reaction is of second order, for  $n = 2$  the value of  $R^2$  being maximum; the rate constants calculated with  $n = 2$  are:

$$k^1_{\text{Ylid1}} = 0.0301 \text{ L/mol s}; k^2_{\text{Ylid1}} = 0.0298 \text{ L/mol s}$$

$$k^1_{\text{Ylid2}} = 0.2325 \text{ L/mol s}; k^2_{\text{Ylid2}} = 0.2362 \text{ L/mol s}$$

By the half-life time method, the values of the rate constants obtained with the equation:  $k_2 = 1/c_0 t_{1/2}$  are:

$$k^1_{\text{Ylid1}} = 0.0297 \text{ L/mol s}; k^2_{\text{Ylid1}} = 0.0292 \text{ L/mol s}$$

$$k^1_{\text{Ylid2}} = 0.2323 \text{ L/mol s}; k^2_{\text{Ylid2}} = 0.2338 \text{ L/mol s}$$

where  $t_{1/2}$  was determined by graphical interpolation, from the kinetic curves.

The agreement between the values of the rate constants obtained by the three methods has confirmed the validity of the calculations, permitting the calculation of the average values:

$$k_{\text{Ylid1}} = 0.0308 \text{ L/mol s}; k_{\text{Ylid2}} = 0.2242 \text{ L/mol s}$$

The thermodynamic study followed the theoretical calculation of the standard formation enthalpies of the participants to the reactions, by means of the MNDO method<sup>10</sup> on which basis the standard reaction enthalpies for these two processes could be calculated (Table III).

The negative values obtained for  $\Delta H^0_{\text{dim}}$  show that the two processes are exothermal, the thermal effect of ylid 2 dimerization being more pronounced.

Variation of Gibbs energy for the dimerization reactions of each of the two ylids can be written:

TABLE III. Standard formation and reaction enthalpies for the two chemical systems taken under study

	$\Delta H_{\text{form.ylid}}^{\circ}/\text{kJ mol}^{-1}$	$\Delta H_{\text{form.dimer}}^{\circ}/\text{kJ mol}^{-1}$	$\Delta H_{\text{dimerization}}^{\circ}/\text{kJ mol}^{-1}$
Ylid 1	325.2	627.5	-22.9
Ylid 2	419.4	454.6	-384.2

$$\Delta G_{\text{dim}}^{\circ} = \Delta H_{\text{dim}}^{\circ} - T\Delta S_{\text{dim}}^{\circ} \quad (4)$$

Taking into account the fact that the structures of the two ylids, as well as of the corresponding dimers, are similar, one may consider that the entropic terms in relation (4) are approximately equal at the same temperature, so that the variations of the Gibbs energies for the two reactions will occur in the same relation as the corresponding variations of enthalpy:

$$\Delta G_{\text{dim},1}^{\circ} - \Delta G_{\text{dim},2}^{\circ} \approx \Delta H_{\text{dim},1}^{\circ} - \Delta H_{\text{dim},2}^{\circ} = 361.3 \text{ kJ/mol} \quad (5)$$

The standard chemical affinities,  $A_{\text{dim}}^{\circ} = -\Delta G_{\text{dim}}^{\circ}$ , whose values are in the following relation:

$$A_{\text{dim},1}^{\circ} < A_{\text{dim},2}^{\circ} \quad (6)$$

prove the higher stability of ylid 1 *versus* ylid 2 in the dimerization reactions,<sup>12</sup> which confirms the conclusions of the kinetic study.

#### CONCLUSIONS

The thermo-kinetic study of the inactivation reactions of 1-methylphthalazinium ylids with  $-\text{NO}_2$  and  $-\text{O}-\text{CH}_3$  substituents in the *p* position of the benzoyl radical bound to the ylidic carbanion permits the following conclusions to be drawn:

1. The dimer's low solubility, experimentally observed, permits a kinetic modeling of the inactivation process as a simple, unilateral reaction;
2. The reaction order,  $n = 2$ , confirms the inactivation reaction to occur through dimerization;
3. The lower reactivity of ylid 1 *versus* ylid 2 in the dimerization reactions – as suggested by the structural characteristics – is confirmed by the values of the rate constants as well as by the relation between the standard chemical affinities of the two reactions.

## ИЗВОД

ТЕРМОКИНЕТИЧКА СТУДИЈА РЕАКЦИЈА ИНАКТИВАЦИЈЕ  
1-МЕТИЛ ФТАЛАЗИНИЈУМ ИЛИДА

MARIA CAPROȘU\*, LUCIA ODOCHIAN\*, ȘT. DIMA\*\*, M. DUMITRAȘ\* and MAGDA PETROVANU\*

\*The "Al. I. Cuza" University, Faculty of Chemistry, Bd. Copou 11, Iasi 6600, Romania and \*\*The "Dunarea de jos" University, Galati, Romania

Овај рад представља термокинетичку студију реакција димеризације 1-метилфталазинијум илида са  $-\text{NO}_2$  (илид 1) и  $-\text{O}-\text{CH}_3$  (илид 2) супституентима у *p* положају бензоил-радикала везаног за илидни карбанјон. На основу експерименталних података одређени су ред реакције и константе брзина. Ред реакције  $n = 2$  потврђује реакцију димеризација илида. Константе брзина димеризације  $k_2 = 3,093 \times 10^{-2} \text{ L/mol s}$  за илид 1 и  $k_2 = 2,16 \times 10^{-1} \text{ L/mol s}$  за илид 2 евидентно указују на већу реактивност илида 2. Овај закључак подржавају и резултати термодинамичке студије хемијских афинитета обе реакције где је добијено да је  $A^{\circ}_{\text{dim},1} < A^{\circ}_{\text{dim},2}$ .

(Примљено 11. октобра 2002, ревидирано 9. јануара 2003)

## REFERENCES

1. I. Zugrăvescu, M. Petrovanu, *N-Ylid Chemistry*, Mc Graw Hill, London 1976
2. St. Dima, I. Mangalagiu, M. Caproșu, M. Petrovanu, *Ann. Sci. Univ. Iasi (sl. c.)* **4** (1996) 151
3. St. Dima, I. Mangalagiu, M. Caproșu, M. Petrovanu, *J. Serb. Chem. Soc.* **62** (1997) 105
4. St. Dima, I. Mangalagiu, M. Caproșu, M. Petrovanu, *Ann. Sci. Univ. Iasi (sl. c.)* **5** (1997) 000
5. A. P. Kreskov, L. N. Bikova, N. A. Kazarian, *Titarea in medium neapos*, Ed. Tehnică, București, 1969
6. D. J. Pietrzyk, C. W. Frank, *Analytical Chemistry*, Academic Press, New York, 1980
7. M. Caproșu, M. Riman, I. Olariu, St. Dima, I. Mangalagiu, M. Petrovanu, *J. Heterocyclic Chem.* **38** (2001) 495
8. M. J. Pilling, P. W. Seakins, *Reaction Kinetics*, Oxford Univ. Press, 1996, p. 9
9. N. Aelenei, Gh. Ionescu, O. Roman, M. I. Popa, *Bul. Inst. Politehnic Iasi XLIV (XLVIII)* (1998) 27
10. J. Sedey, *Semi-Empirical Methods of Quantum Chemistry*, Wiley, New York 1985, pp. 130 – 135
11. St. Dima, I. Mangalagiu, M. Caproșu, M. Petrovanu, *Ann. Sci. Univ. Iasi (sl. c.)* **5** (1997) 001
12. G. Bourceanu, P. Joulain, L. Gbahoue, V. Locquet, *Entropie* **170** (1992) 17.