CALCULATION OF ISOKINETIC TEMPERATURE OF NON-CATALYZED HYDROLYSIS OF SUBSTITUTED 3-(N-METHYLCARBAMOYL)-1,3-DIPHENYL-TRIAZENES

Oldřich PYTELA, Miroslav VEČEŘA and Pavel VETEŠNÍK

Department of Organic Chemistry,
Institute of Chemical Technology, 532 10 Pardubice

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Temperature dependence of kinetics of non-catalyzed hydrolysis of substituted 3-(N-methyl-carbamoyl)-1,3-diphenyltriazenes has been measured. An optimized calculation method has been suggested for calculation of the isokinetic temperature and the experimental data have been evaluated. In all the cases it has been found that the hypothesis of common intersection of the straight lines log k *vs* $1/T$ is rejected at the significance level $\alpha = 0{\cdot}05$, but, within approximate validity of the isokinetic hypothesis the isokinetic relation can be considered to be fulfilled in the given reaction series. The change of the reaction constant ϱ connected with the change of the reaction mechanism shows a statistically significant correspondence with the change of the isokinetic temperature.

Kinetics and mechanism of the non-catalyzed hydrolysis of substituted 3-(N-methyl-carbamoyl)-1,3-diphenyltriazenes

$$\underset{\displaystyle \qquad\qquad\quad |\atop \qquad\qquad\quad CO{-}NH{-}CH_3}{X{-}C_6H_4{-}N{=}N{-}N{-}C_6H_4{-}X} \xrightarrow{H_2O} \underset{OH^{(-)}}{X{-}C_6H_4{-}N_2^{(+)}} + \underset{\displaystyle |\atop CO{-}NH{-}CH_3}{NH{-}C_6H_4{-}X}$$

were described in our previous papers[1,2]. The Hammett dependence was also evaluated but without verification of the isokinetic relation.

The problem of calculation of the isokinetic temperature (β) was extensively elaborated by Exner[3-9]. From the computation viewpoint the problem consists in finding such a constant x_0 ($= \beta^{-1}$) in the equation system (*1*), that the relation (*2*) is fulfilled in which x_{ij}($= T_{ij}^{-1}$) and y_{ij} ($= \log k_{ij}$) are

$$y_{ij} = y_0 + b_i(x_{ij} - x_0) \tag{1}$$

$$S = \sum_{i=1}^{n} \sum_{j=1}^{m_i} w_{ij}(y_{ij} - f_i(x_{ij}, \Theta))^2/p = \min \tag{2}$$

experimental values of the j-th measurement in the i-th series, x_0 and y_0 are coordinates of the common intersection of n straight lines, p is number of degrees of freedom, and f_i is defined by the relation (3). The weights w_{ij} in Eq. (2) are determined by the relation (4). Calculation of x_0 in the system (1) represents a

$$f_i(x_{ij}, \hat{\Theta}) = \hat{y}_0 + \hat{b}_i(x_{ij} - \hat{x}_0) \tag{3}$$

$$w_{ij} = (\sum_{i=1}^{n} m_i)/\sigma_{ij} \sum_{i=1}^{n} \sum_{j=1}^{m_i} \sigma_{ij}^{-2} \tag{4}$$

non-linear problem with one non-linear parameter which can be effectively found by one-dimensional optimization and the remaining parameters can be calculated by the method of linear regression. The covariance matrix of the parameters can be defined by the likelihood function L, because it holds that

$$-[\partial^2 \ln L/\partial\Theta_\alpha\, \partial\Theta_\beta]^{-1} \tag{5}$$

is the covariance matrix of the parameters[10], Θ_α and Θ_β representing the individual parameters. Derivative of the likelihood function can be expressed by Eq. (6) in which S is given by Eq. (2).

$$\partial^2 \ln L/\partial\Theta_\alpha\, \partial\Theta_\beta = -\sum_{i=1}^{n} \sum_{j=1}^{m_i} w_{ij}(\partial f_i(x_{ij}, \hat{\Theta})/\partial\Theta_\beta)\,(\partial f_i(x_{ij}, \hat{\Theta})/\partial\Theta_\beta)/S\,. \tag{6}$$

Shimulis suggested three criteria[11,12] based on analysis of dispersion variance for statistical evaluation of existence of the isokinetic temperature. These criteria can be summarized in the formula (7), where $\nu_1 = n - 1$, $\nu_2 = \sum_{i=1}^{n} m_i - 2n$.

$$F(\nu_1, \nu_2) = \nu_2[\sum_{i=1}^{n}(z_i - \bar{z})^2]/\nu_1[\sum_{i=1}^{n}(m_i - 2)\, s_{z_i}^2] \tag{7}$$

The first criterion tests whether the straight lines y_{ij} *vs* x_{ij} intersect, within experimental error, in the point x_0, y_0 ($z_i = f_i(x_0, \hat{\Theta})$). The second criterion ($z_i = f_i(0, \hat{\Theta})$) and the third criterion ($z_i = b_i$) test whether the straight lines intersect in the point $x_0 = 0$ (an isentropic reaction) or are parallel, because in these cases the isokinetic temperature cannot be determined. Exner[5,7] approaches this problem in another way, testing whether there is isokinetic temperature in the given experimental set within approximate validity of the isokinetic relation. For this purpose he compares the standard deviations s_0 (from regression by a family of lines with intersection x_0, y_0) and s_{00} (sum of standard deviations of the Arrhenius straight lines). Extent of correlation between the experimental data within the isokinetic relation can be evaluated according to the criterion defined by Eq. (8)

TABLE I

Temperature Dependence of Hydrolysis Rate Constants of Substituted 3-(N-Methylcarbamoyl)--1,3-diphenyltriazenes at pH 3·56

T	*I*, X = H		T	*II*, X = 4-CH_3		T	*III*, X = 4-Cl	
°C	k, s^{-1}	s_k, s^{-1}	°C	k, s^{-1}	s_k, s^{-1}	°C	k, s^{-1}	s_k, s^{-1}
25	5·491 . 10^{-4}	6·906 . 10^{-6}	20	5·367 . 10^{-4}	1·214 . 10^{-5}	25	1·867 . 10^{-4}	8·131 . 10^{-6}
30	1·093 . 10^{-3}	2·896 . 10^{-5}	20	5·032 . 10^{-4}	1·208 . 10^{-5}	25	1·809 . 10^{-4}	4·483 . 10^{-6}
35	1·800 . 10^{-3}	4·231 . 10^{-5}	25	1·048 . 10^{-3}	9·770 . 10^{-6}	30	3·910 . 10^{-4}	8·541 . 10^{-6}
45	5·331 . 10^{-3}	1·357 . 10^{-4}	25	1·007 . 10^{-3}	2·431 . 10^{-5}	35	6·233 . 10^{-4}	1·103 . 10^{-5}
50	8·521 . 10^{-3}	2·164 . 10^{-4}	25	1·138 . 10^{-3}	3·029 . 10^{-5}	35	6·978 . 10^{-4}	8·239 . 10^{-6}
55	1·773 . 10^{-2}	6·534 . 10^{-4}	30	1·660 . 10^{-3}	3·228 . 10^{-5}	40	1·231 . 10^{-3}	1·019 . 10^{-5}
60	2·798 . 10^{-2}	1·210 . 10^{-3}	30	1·700 . 10^{-3}	3·653 . 10^{-5}	40	1·206 . 10^{-3}	1·848 . 10^{-5}
			35	2·489 . 10^{-3}	2·465 . 10^{-5}	45	2·398 . 10^{-3}	5·127 . 10^{-5}
			35	2·548 . 10^{-3}	2·818 . 10^{-5}	45	2·290 . 10^{-3}	5·056 . 10^{-5}
			40	4·053 . 10^{-3}	1·559 . 10^{-4}			
			40	4·212 . 10^{-3}	7·985 . 10^{-5}			

	IV, X = 4-Br			*V*, X = 3-Cl			*VI*, X = 3-Br	
30	2·986 . 10^{-4}	5·971 . 10^{-6}	35	2·447 . 10^{-4}	1·330 . 10^{-5}	35	2·010 . 10^{-4}	6·119 . 10^{-6}
30	2·385 . 10^{-4}	5·189 . 10^{-6}	35	2·340 . 10^{-4}	1·169 . 10^{-5}	40	3·833 . 10^{-4}	1·109 . 10^{-5}
35	4·928 . 10^{-4}	1·215 . 10^{-5}	40	4·828 . 10^{-4}	8·021 . 10^{-6}	40	4·123 . 10^{-4}	7·098 . 10^{-6}
35	4·318 . 10^{-4}	4·835 . 10^{-6}	40	4·903 . 10^{-4}	1·061 . 10^{-5}	45	7·397 . 10^{-4}	1·289 . 10^{-5}
40	7·447 . 10^{-4}	1·009 . 10^{-5}	45	8·492 . 10^{-4}	1·126 . 10^{-5}	45	8·060 . 10^{-4}	1·439 . 10^{-5}
45	1·313 . 10^{-3}	2·447 . 10^{-5}	50	1·445 . 10^{-3}	2·708 . 10^{-5}	50	1·298 . 10^{-3}	1·373 . 10^{-5}
45	1·487 . 10^{-3}	4·233 . 10^{-5}	50	1·560 . 10^{-3}	3·538 . 10^{-5}	50	1·426 . 10^{-3}	1·378 . 10^{-5}
50	2·408 . 10^{-3}	4·260 . 10^{-5}	55	2·792 . 10^{-3}	3·948 . 10^{-5}	55	2·793 . 10^{-3}	3·070 . 10^{-5}
50	2·495 . 10^{-3}	3·948 . 10^{-5}	55	2·697 . 10^{-3}	5·248 . 10^{-5}	55	2·603 . 10^{-3}	4·802 . 10^{-5}

T	*VII*, X = 3-F		T	*VIII*, X = 3-CH_3SO_2		T	*XI*, X = 4-CN	
°C	k, s^{-1}	k_k, s^{-1}	°C	k, s^{-1}	k_k, s^{-1}	°C	k, s^{-1}	s_k, s^{-1}
35	3·162 . 10^{-4}	2·585 . 10^{-6}	40	2·195 . 10^{-4}	1·446 . 10^{-6}	35	1·840 . 10^{-4}	1·395 . 10^{-6}
35	3·698 . 10^{-4}	9·508 . 10^{-6}	40	2·182 . 10^{-4}	1·757 . 10^{-6}	35	1·851 . 10^{-4}	1·021 . 10^{-6}
40	4·498 . 10^{-4}	8·963 . 10^{-6}	45	3·743 . 10^{-4}	2·600 . 10^{-6}	40	3·620 . 10^{-4}	2·667 . 10^{-6}
40	4·568 . 10^{-4}	1·050 . 10^{-5}	45	3·768 . 10^{-4}	3·553 . 10^{-6}	40	3·685 . 10^{-4}	9·153 . 10^{-7}
45	1·047 . 10^{-3}	1·302 . 10^{-5}	50	7·666 . 10^{-4}	3·747 . 10^{-6}	45	5·560 . 10^{-4}	2·292 . 10^{-6}
45	1·059 . 10^{-3}	2·295 . 10^{-5}	50	7·475 . 10^{-4}	3·087 . 10^{-6}	45	6·657 . 10^{-4}	2·208 . 10^{-6}
50	1·795 . 10^{-3}	1·775 . 10^{-5}	55	1·226 . 10^{-3}	3·688 . 10^{-6}	50	1·391 . 10^{-3}	6·477 . 10^{-6}
50	1·833 . 10^{-3}	1·833 . 10^{-5}	55	1·245 . 10^{-3}	5·385 . 10^{-6}	50	1·365 . 10^{-3}	7·677 . 10^{-6}
55	2·648 . 10^{-3}	5·873 . 10^{-5}	60	1·977 . 10^{-3}	1·308 . 10^{-5}	55	2·323 . 10^{-3}	1·672 . 10^{-5}
55	2·817 . 10^{-3}	4·577 . 10^{-5}	60	1·928 . 10^{-3}	1·948 . 10^{-5}	55	2·317 . 10^{-3}	1·803 . 10^{-5}

TABLE I
(*Continued*)

IX, X = 3-CN			*X*, X = 3-NO_2			*XII*, X = 4-NO_2		
40	$1{\cdot}394 \cdot 10^{-4}$	$1{\cdot}329 \cdot 10^{-6}$	40	$1{\cdot}082 \cdot 10^{-4}$	$1{\cdot}169 \cdot 10^{-6}$	35	$3{\cdot}163 \cdot 10^{-4}$	$1{\cdot}767 \cdot 10^{-5}$
40	$1{\cdot}351 \cdot 10^{-4}$	$1{\cdot}895 \cdot 10^{-6}$	40	$1{\cdot}029 \cdot 10^{-4}$	$1{\cdot}037 \cdot 10^{-6}$	35	$3{\cdot}388 \cdot 10^{-4}$	$1{\cdot}953 \cdot 10^{-5}$
45	$2{\cdot}607 \cdot 10^{-4}$	$2{\cdot}132 \cdot 10^{-6}$	45	$2{\cdot}089 \cdot 10^{-4}$	$8{\cdot}658 \cdot 10^{-6}$	40	$6{\cdot}032 \cdot 10^{-4}$	$1{\cdot}419 \cdot 10^{-5}$
45	$2{\cdot}628 \cdot 10^{-4}$	$2{\cdot}410 \cdot 10^{-6}$	45	$2{\cdot}140 \cdot 10^{-4}$	$3{\cdot}703 \cdot 10^{-6}$	40	$6{\cdot}680 \cdot 10^{-4}$	$2{\cdot}030 \cdot 10^{-5}$
50	$5{\cdot}407 \cdot 10^{-4}$	$3{\cdot}082 \cdot 10^{-6}$	50	$3{\cdot}855 \cdot 10^{-4}$	$4{\cdot}767 \cdot 10^{-6}$	45	$1{\cdot}506 \cdot 10^{-3}$	$5{\cdot}733 \cdot 10^{-5}$
50	$5{\cdot}580 \cdot 10^{-4}$	$6{\cdot}163 \cdot 10^{-6}$	50	$4{\cdot}445 \cdot 10^{-4}$	$7{\cdot}101 \cdot 10^{-6}$	45	$1{\cdot}337 \cdot 10^{-3}$	$5{\cdot}260 \cdot 10^{-5}$
55	$8{\cdot}523 \cdot 10^{-4}$	$1{\cdot}987 \cdot 10^{-5}$	55	$6{\cdot}918 \cdot 10^{-4}$	$6{\cdot}423 \cdot 10^{-6}$	45	$1{\cdot}306 \cdot 10^{-3}$	$3{\cdot}845 \cdot 10^{-5}$
55	$8{\cdot}693 \cdot 10^{-4}$	$1{\cdot}499 \cdot 10^{-5}$	55	$6{\cdot}975 \cdot 10^{-4}$	$2{\cdot}677 \cdot 10^{-6}$	45	$1{\cdot}309 \cdot 10^{-3}$	$3{\cdot}615 \cdot 10^{-5}$
60	$1{\cdot}450 \cdot 10^{-3}$	$4{\cdot}473 \cdot 10^{-5}$	60	$1{\cdot}095 \cdot 10^{-3}$	$9{\cdot}208 \cdot 10^{-6}$	50	$2{\cdot}603 \cdot 10^{-3}$	$5{\cdot}177 \cdot 10^{-5}$
60	$1{\cdot}437 \cdot 10^{-3}$	$3{\cdot}711 \cdot 10^{-5}$	60	$1{\cdot}147 \cdot 10^{-3}$	$6{\cdot}931 \cdot 10^{-6}$	50	$2{\cdot}263 \cdot 10^{-3}$	$5{\cdot}463 \cdot 10^{-5}$
60	$1{\cdot}730 \cdot 10^{-3}$	$4{\cdot}468 \cdot 10^{-5}$	60	$1{\cdot}131 \cdot 10^{-3}$	$4{\cdot}537 \cdot 10^{-5}$	55	$4{\cdot}483 \cdot 10^{-3}$	$2{\cdot}323 \cdot 10^{-5}$
			60	$1{\cdot}145 \cdot 10^{-3}$	$1{\cdot}903 \cdot 10^{-5}$	55	$4{\cdot}685 \cdot 10^{-3}$	$2{\cdot}253 \cdot 10^{-5}$

$$\psi = \Big[\sum_{i=1}^{n} m_i \sum_{i=1}^{n} \sum_{j=1}^{m_i} w_{ij}(y_{ij} - f_i(x_{ij}, \hat{\Theta}))^2 \Big/ \Big(\sum_{i=1}^{n} m_i - n - 2\Big) \,. \\ \cdot \sum_{i=1}^{n} \sum_{j=1}^{m_i} w_{ij}(y_{ij} - \bar{y})^2\Big]^{1/2} , \qquad (8)$$

where $\bar{y}$ stands for arithmetic mean. Magnitude of the criterion ψ is judged according to the convention[13].

EXPERIMENTAL

Synthesis of the compounds studied and the measurements methods were described in the previous papers[1,2]. The measurements were carried at pH 3·56 in phthalate buffer, the temperature in the cell was measured with accuracy of $\pm 0{\cdot}1$°C. The experimental results were treated by the Exner procedure[7] modified by the use of the effective optimization procedure in a broad temperature range, and the results were complemented with the covariance matrix of parameters. The minimum value of S in Eq. (2) with respect to the parameter x_0 was searched for within the interval

$$1\,000x_0 \in \langle -7{\cdot}00;\ 10{\cdot}5 \rangle \qquad (9)$$

which was divided into 0·5 unit sections. In the individual points x_0^k we calculated the residual sums of squares S_k (Eq. (2)), and the point x_k^0 fulfilling the condition (10) was chosen to be

$$S_k(x_{ij}, x_0^k) < S_l(x_{ij}, x_0^l) \; ; \quad l = 1, 2, \ldots, 36 \; ; \quad l \neq k \qquad (10)$$

the centre of a new interval $x_0^{k-1}; x_0^{k+1}$. In this interval we used the Fibonacci optimization with 35 Fibonacci numbers. The covariance matrix was calculated according to the relations

(*6*) and (*2*), the criteria F_1, F_2, F_3 were calculated according to Eq. (*7*), and the criterion ψ was calculated by Eq. (*8*). The calculations were carried out in the FORTRAN IV language using the ADT 4100 computer for four groups of the substitution derivatives (*I—IX*, *X—XII*, *I—X*, *I—XII*; Table I) and for different (W) and unit (U) weights.

RESULTS AND DISCUSSION

To test the suggested calculation procedure we used an example from literature[7,14]. The values obtained by us ($\beta = -1739$ K, $s_0 = 0.088$, $s_{00} = 0.096$, $s_\beta = 623$ K,

TABLE II

Isokinetic Temperatures and Statistical Criteria for Non-Catalyzed Hydrolysis of Substituted 3-(N-Methylcarbamoyl)-1,3-diphenyltriazenes *I—XII* in the Series *I—IV*

Series	I_W	I_U	II_W	II_U	III_W	III_U	IV_W	IV_U
n	9	9	3	3	10	10	12	12
$\sum m_i$	85	85	34	34	95	95	119	119
β, K	501·7	597·4	—186·1	204·8	531·2	618·0	705·9	618·0
s_β, K	61·2	95·0	51·0	28·9	60·5	86·8	193·9	89·9
F_1	3·38	4·90	3·15	0·03	3·33	4·99	6·00	7·35
F_2	6·88	6·75	4·78	8·22	6·52	6·68	8·04	8·73
F_3	11·62	10·59	2·46	3·45	11·60	10·99	12·45	12·21
$F_{0.95}$	2·08	2·08	3·34	3·34	2·01	2·01	1·89	1·89
$10^2 s_0$	2·76	4·10	2·86	2·82	2·56	3·92	2·93	4·25
$10^2 s_{00}$	2·86	4·10	5·51	5·13	2·84	3·81	3·00	3·61
$10^2 \psi$	8·14	9·16	8·69	6·59	6·88	8·66	8·70	9·53

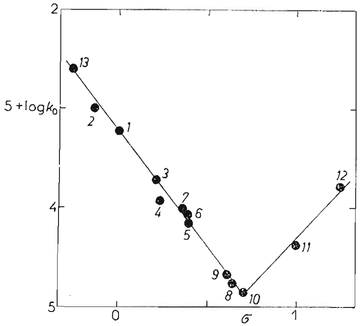

FIG. 1

Dependence of Logarithms of Rate Constants of Non-Catalyzed Hydrolysis of 3-(N-Methylcarbamoyl)-1,3-diphenyltriazenes on the Hammett σ Constants (for numbers see Table I, 13, $X = 4\text{-}CH_3O$)

$F_1 = 0{\cdot}34$, $F_2 = 1{\cdot}19$, $F_3 = 23{\cdot}9$ ($F_{0.95} = 2{\cdot}00$)) agree well with those given in literature[7] ($\beta = -1740$ K, $s_0 = 0{\cdot}089$, $s_{00} = 0{\cdot}096$). The testing criteria show that the intersection of the lines (*1*) is significant at the significance level $\alpha = 0{\cdot}05$, the value x_0 being equal to zero with statistical significance at the same significance level (the isentropic reaction).

Table I gives the hydrolysis rate constants of the substituted 3-(N-methylcarbamoyl)-1,3-diphenyltriazenes at various temperatures. The results of the repeated measurements showed the measurement error $\delta = 0{\cdot}04$, and, therefore, for testing the results we chose the significance level $\alpha = 0{\cdot}05$. Table II summarizes the results of calculation of isokinetic temperature and statistical criteria arranged into four series. These series were formed on the basis of dependence of logarithm of rate constant of the non-catalyzed hydrolysis of the substrates studied on the Hammett σ constants (Fig. 1) with the aim to verify whether change of the reaction constant ϱ is accompanied by simultaneous change of isokinetic temperature. From Table II it can be seen that none of the series studied is isentropic (the criterion F_2). The calculation of isokinetic temperature is meaningless for three substituted derivatives with $\sigma > 0{\cdot}7$ (series $\mathrm{II_U}$), because the lines described by Eq. (*1*) are parallel with statistical significance (criterion F_3) at the level $\alpha = 0{\cdot}05$. Hence, these results cannot be used for direct evaluation of differences of the estimates of isokinetic temperatures in the series I and II. The criterion F_1 in Table II indicates statistical insignificance of existence of intersection of the lines (*1*) at the significance level $\alpha = 0{\cdot}05$ in the series I, III and IV, although all the other criteria are fulfilled. On the contrary, in none of these series the value s_{00} is significantly greater than δ (the Arr-

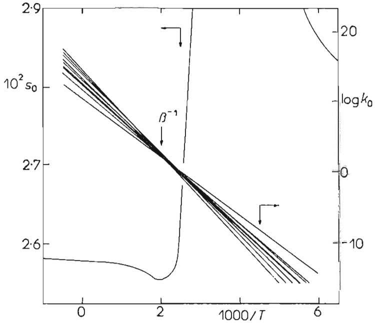

FIG. 2

Isokinetic Relation for Non-Catalyzed Hydrolysis of 3-(N-Methylcarbamoyl)-1,3-diphenyltriazenes henius relation is obeyed), and also s_0 is not significantly greater than s_{00}, and thus the isokinetic hypothesis cannot be rejected. In all the cases the correlation can be described as good on the basis of the criterion ψ according to the convention[13]. Within approximate validity of the isokinetic relation it is possible to consider this relation to be fulfilled with the accuracy s_0 in the studied series. To judge whether the 3-nitro derivative *X* has a common intersection with the other derivatives *I*–*IX* we used the criterion

$$t = \left|g_0(x_0, \hat{\Theta}^0) - n^{-1} \sum_{i=1}^{n} g_i(x_0, \hat{\Theta}^i)\right| / [v_2^{-1} \sum_{i=1}^{n} (m_i - 2)\, s_i^2]^{1/2}\,, \qquad (11)$$

in which

$$g_i(\hat{x}_0, \hat{\Theta}^i) = a_i + b_i \hat{x}_0 \qquad (12)$$

means the value of regression function of the *i*-th line in the point x_0, s_i is the standard deviation of the assessment g_i. The criterion (*11*) has, under the presumption of validity of the hypothesis tested, *t* distributions with v_2 $(= \sum_{i=1}^{n+1} m_i - 2(n + 1))$ degrees of freedom. The hypothesis was rejected at the significance level $\alpha = 0{\cdot}05$ in both the calculation with different weights ($t_W = 1{\cdot}22$, $t_{0.95} = 1{\cdot}67$) and that with the same ones ($t_U = 1{\cdot}24$). Hence the estimate of the isokinetic temperature calculated with involvement of the derivative *X* will not statistically differ, and the intermediate derivative *X* can thus be added to the other derivatives *I*–*IX* (series III, Table II). The same criterion (*11*) was used to test the hypothesis whether also 4-cyano (*XI*) and 4-nitro (*XII*) derivatives (which have $\varrho > 0$ (Fig. 1) in contrast to the foregoing substrates) give the same regression value at the point x_0 (determined for the compounds *I*–*X*) as the mean of the regression values at the point x_0 of the independent lines *I*–*X*. The hypothesis was rejected at the significance level $\alpha = 0{\cdot}05$ for the derivative *XI* ($t_U = 3{\cdot}14$, $t_{0.95} = 1{\cdot}67$) in calculation with the same weights, but it was not rejected for the same derivative with different weights ($t_W = 1{\cdot}09$). For the derivative *XII* the hypothesis (*11*) was rejected at the significance level $\alpha = 0{\cdot}05$ in the both cases ($t_W = 5{\cdot}24$, $t_U = 5{\cdot}79$). From these results it can be concluded that the derivatives *XI* and *XII* with the reaction constant $\varrho > 0$ have different isokinetic temperature from that of the derivatives *I*–*X*. According to expectation the isokinetic temperature is characteristical of one type of mechanism and rate-limiting step in a given substituent series. Change of the isokinetic temperature corresponds with change in linearity of the Hammett relation.

From the point of view of classification of reaction series according to relation between the activation parameters[4] the hydrolysis of the studied compounds represents the most common case of compensation ($\beta > T_{exp}$). The isokinetic relation is illustrated in Fig. 2 (series III).

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