KINETICS AND MECHANISM OF ACID CATALYZED DECOMPOSITION OF 1-PHENYL-3,3-DIALKYLTRIAZENES

Miroslav LUDWIG, Pavla VALASKOVA and Oldrich PYTELA
Department of Organic Chemistry,
University of Chemical Technology, 532 10 Pardubice, The Czech Republic

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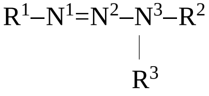
Five model 1-phenyl-3,3-dialkyltriazenes (methyl, ethyl, 2-propyl, butyl, cyclohexyl) have been synthesized and their acid-catalyzed decomposition kinetics have been investigated spectrophotometrically in aqueous ethanol (40 vol.%) with pivalic acid as the catalyst. The results show that the rate-determining step is catalyzed by the proton. The decrease in the observed rate constant at higher concentrations of pivalic acid is explained by the formation of an unreactive complex of the nondissociated acid and respective triazene. The steric effect of alkyl groups on the catalytic rate constants is discussed.

Triazenes of general formula *I* where R^1 is most frequently an aryl, R^2 is alkyl, and R^3 is alkyl, aryl, acyl, halogen, hydroxyl, or hydrogen, are decomposed at the conditions of acid catalysis in various solvents[1 – 21]. The decomposition products involve the diazonium salts and corresponding complementary compounds having a bond N^3–H instead of N^3–N^2. From the point of view of mechanism of acid-catalyzed decomposition, the triazene molecule is interesting by the fact that, in principle, each of the three nitrogen atoms can be protonated. The quantum-chemical calculations indicate either the same probability of protonation at N^1 and N^3 (ref.[22]) or preferable protonation at N^1 (ref.[23]). The triazene chain is split only in the case of the protonation at the N^3 atom, whereas the protonations of the other nitrogen atoms mostly represent side equilibria[19].



$$R^1–N^1{=}N^2–\underset{\displaystyle R^3}{\underset{|}{N^3}}–R^2$$

I

As for the catalysis type, this can be either the specific acid catalysis involving a pre-equilibrium – the protonation of substrate – and subsequent decomposition to products or the general acid catalysis involving simultaneous formation of N^3–H bond and splitting of N^3–N^2 bond. In literature there is no unequivocal conformity in the view on the mechanism of acid-catalyzed decomposition of triazenes, the type of mechanism obviously also depends on the character of substituents R^1, R^2, R^3 (formula *I*). Some papers, especially the older ones, prefer the specific catalysis going by the monomolecular mechanism A1 (refs[1 – 5,12,14]). On the other hand, a number of results observed indicate the bimolecular mechanism of A-S_E2 type with general acid catalysis[11]: beside the criterion of isokinetic temperature also the salt effects in the decomposition of 3-acetyl-1,3-diphenyltriazenes and 3-(*N*-methylcarbamoyl)-1,3-diphenyltriazenes (ref.[10]) indicating the existence of ion pairs, hence an easy splitting of the N^2–N^3 bond. The mathematical modelling of decomposition mechanism of 3-methyl-1,3-diphenyltriazenes in buffers formed by general acids indicates the general catalysis by A-S_E2 mechanism involving the proton-catalyzed splitting[17]. The investigation of substituent effects in the latter substrate types did not bring unequivocal results with respect to the reaction course[16]. Investigations of the effect of medium on decomposition of 1,3-bis(4-methylphenyl)triazene catalyzed with trichloroacetic acid in amphiprotic and aprotic media[19 – 21] revealed, in various types of solvents, three types of the dependence between the observed rate constant and concentration of the catalyst trichloroacetic acid. The fastest reactions were those with the proton, slower ones with undissociated acid, and the slowest with the acid dimer. The reaction rate in the individual media depended on the predominant form of the catalyst acid in the given medium. The reactions with the undissociated acid, the proton, as well as that with the acid dimer proceed in this case by the mechanism of general acid catalysis.

The aim of the present work is to study the effect of magnitude of alkyl groups bound to N^3 atom upon the kinetics of acid catalyzed decomposition of 1-phenyl-3,3-dialkyltriazenes *I* (R^1 = phenyl, $R^2 = R^3$ = methyl, ethyl, isopropyl, butyl, cyclohexyl) in the medium of 40 vol.% aqueous ethanol and to verify the mechanism of general acid catalysis at these conditions. For the catalyst acid we chose the relatively bulky pivalic acid.

EXPERIMENTAL

Spectral measurements. The electronic spectra were measured in 40 vol.% aqueous ethanol using a Specord M-40 apparatus. The mass spectra were measured with a Kratos MS 25RSA apparatus using the EI technique in the GC/MS arrangement. The ^{1}H NMR and ^{13}C NMR spectra of the substances were measured in deuteriochloroform using a JEOL JNM-FX 100 or a Bruker AM-400 apparatus at 300 and 330 K, respectively.

1-Phenyl-3,3-dialkyltriazenes were prepared by the reaction of benzenediazonium chloride with the corresponding secondary amine[24]. A solution of 0.3 mol amine in 250 ml water with ice (the preparation procedure *A*) was treated with 75 g (ca 0.8 mol) sodium carbonate and the suspension obtained was then treated with cold solution of 0.3 mol benzenediazonium chloride added during 20 min. The diazonium solution was obtained by diazotizing 28 g (0.3 mol) aniline with 21 g (0.3 mol) sodium nitrite in 200 ml 20% hydrochloric acid. The reaction mixture was stirred for another 30 min at 5 – 10 °C. In the cases of water insoluble amines (the preparation procedure *B*), the solution of benzenediazonium chloride (0.3 mol) was mixed with a suspension or solution of hydrochloride of the corresponding amine (0.3 mol). The mixture obtained was treated with a cold solution of 90 g sodium carbonate (ca 1 mol) in 250 ml water added with constant stirring, and the reaction suspension was then stirred for another 30 min. The products were purified by chromatography on alumina column with ethyl acetate–chloroform 10 : 1 as the mobile phase. The preparation procedure of the individual model triazenes, yields, and elemental analyses are given in Table I.

Determination of concentration and pK_{HA} *of pivalic acid*. The concentration of catalyst acid and its pK_{HA} in 40 vol.% aqueous ethanol were determined by potentiometric titration using an automatic titrator Radiometer RTS 622 and methanolic tetrabutylammonium hydroxide (0.1 mol dm^{-3}) as the titrant. The electrodes used for the measurements were identical with those in our earlier works[25]. Benzoic acid was chosen for the standard (pK_{HA} 5.76 in 40% ethanol[26]). The solutions with the same concentrations of proton at different concentrations of pivalic acid (used in the case of dicyclohexyl derivative) were prepared by titrating the solutions of acid with a 20% solution of NaOH in 40% ethanol to the pH (mV) value of the least concentrated solution used.

Kinetic measurements. The solution of pivalic acid of definite concentration was thermostatted in a quartz cell at 25 ± 0.1 °C for 10 min. Then, using a Hamilton syringe, a solution of respective triazene in dioxane (6 μl ca $5 . 10^{-3}$ mol dm^{-3}) was added into the cell and the solution was mixed. The concentration decrease of starting triazene was monitored at the wavelength of the longestwave maximum (Table II) during a period of three halflives.

Treatment of results. The kinetic curves were evaluated by means of our own optimization program[27]. The statistical treatment of the results by nonlinear regression, principal components analysis, and linear regression was carried with the use of our own programs on a PC-AT.

TABLE I
Preparation methods, yields, and elemental analyses of synthesized 1-phenyl-3,3-dialkyltriazenes $C_6H_5N=N-NR_2$

R	Formula (M.w.)	Method Yield, %	Calculated/Found %C	Calculated/Found % H	Calculated/Found % N	M.p., °C
Methyl (Me)	$C_8H_{11}N_3$	*A*	64.75	7.65	27.91	oil
	(149.2)	60	64.43	7.38	28.18	
Ethyl (Et)	$C_{10}H_{15}N_3$	*A*	67.63	8.69	23.64	oil
	(177.2)	73	67.79	8.47	23.73	
Isopropyl (*i*-Pr)	$C_{12}H_{29}N_3$	*A*	69.93	9.23	20.22	39 – 40
	(215.4)	48	70.24	9.27	20.49	
Butyl (Bu)	$C_{14}H_{23}N_3$	*A*	71.81	9.98	18.22	oil
	(233.4)	74	72.10	9.87	18.03	
Cyclohexyl (cHx)	$C_{18}H_{27}N_3$	*B*	75.41	9.83	14.67	133 – 134
	(285.4)	27	75.79	9.47	14.73	

RESULTS AND DISCUSSION

Spectral data (UV-VIS, MS, ^{1}H NMR, ^{13}C NMR) of the 1-phenyl-3,3-dialkyltriazenes prepared are presented in Table II. The mass spectra showed a similar fragmentation in all the model substrates. In all the cases the most intensive fragment is C_6H_5 (m/z = 77), most spectra exhibit the fragment $C_6H_5N_2$ (m/z = 105) formed by N^2–N^3 bond rupture. This bond splitting also produces the fragments R^1R^2N (m/z = 44, 72, 100, 128, 180) which further decompose to give the RNH fragments (m/z = 30, 44, 58, 72, 98) and R fragments (m/z = 15, 29, 43, 57, 83). The NMR spectra proved the presumed structure of triazenes. In addition, the ^{1}H NMR spectra of the dimethyl and dibutyl derivatives showed the equivalence of both alkyl groups with regard to chemical shifts, which corresponds to rapid rotation around the N^2–N^3 bond. On the other hand, the CH signals of the isopropyl derivative are broadened at 300 K and those of the cyclohexyl derivative are very broad. At 330 K they become more narrow, which confirms hindered

TABLE II
Spectral characteristics (UV-VIS, MS, NMR) of synthesized 1-phenyl-3,3-dialkyltriazenes $C_6H_5N{=}N{-}NR_2$

R	λ_{max}, nm	m/z, %	δ, ppm (T = 300 K)
Me	310	44 (8), 51 (32), 77 (100), 78 (40), 105 (90), 120 (8), 149 (63)	^{1}H arom: 7.51 – 7.00 m, 5 H aliph: 3.35, 6 H
Et	312	72 (8), 77 (100), 78 (12), 105 (42), 177 (15)	
i-Pr	318	43 (32), 51 (20), 58 (44), 77 (100), 78 (25), 80 (12), 100(40), 105 (63), 120 (8), 205 (25)	^{1}H arom: 7.47 – 7.00 m, 5 H aliph: 4.58, 2 H (2 CH), 1.29, 12 H (4 CH_3, ^3J(H,H) = 6.8) ^{13}C arom: 151.7 s, 128.7 d, 124.7 s 120.3 s aliph: 77.0 m
Bu	313	51 (12), 57 (16), 77 (100), 78 (40), 84 (14), 86 (26), 93 (11), 105 (92), 120 (8), 128 (28), 148 (8), 233 (39)	^{1}H arom: 7.42 – 7.00 m, 5 H aliph: 3.68, 4 H (2 CH_2), 1.65, 4 H (2 CH_2), 1.10, 4 H (CH_2), 0.93, 12 H (2 CH_3)
cHx	317	55 (18), 77 (100), 83 (18), 83 (18), 98 (25), 138 (15), 180 (38), 285 (12)	^{1}H arom: 7.46 – 7.00 m, 5 H aliph: 4.1 2 H (2 CH), 1.90 – 1.00, 20 H (10 CH_2) ^{13}C arom: 151.7 s, 128.6 d, 124.5 s, 120.3 s alif: 77.0 m, 25.8 d

rotation with bulky substituents. These conclusions are also confirmed by the signals in ^{13}C NMR spectra of isopropyl and cyclohexyl derivatives at 300 and 330 K.

Table III gives the observed rate constants k_{obs} of the acid-catalyzed decomposition of the model triazenes in 40 vol.% aqueous ethanol at 25 °C. The experimental values obtained exhibit diminishing increases in the observed rate constant with increasing concentration of pivalic acid, and, beginning from the acid concentration of 0.34 – 0.56 mol dm^{-3} (depending on the substituents of substrate) k_{obs} even decreases. The facts mentioned can be seen in Fig. 1 (full circles).

From the survey in the introduction of this paper it follows that the decomposition of triazene can take place by several basic mechanisms. In the first one the triazene (T) is split into the products (P) by the A-S_E2 mechanism in a reaction of the triazene with

TABLE III
Observed rate constants ($k_{obs,}$ s^{-1}) of decomposition of 1-phenyl-3,3-dialkyltriazenes $C_6H_5N{=}N{-}NR_2$ in 40 vol.% aqueous ethanol at 25 °C at various concentrations of catalyst acid

c . 10^3 mol dm^{-3}	k_{obs} . 10^3, s^{-1}				
	Me	Et	*i*-Pr	Bu	cHx
0.0837	0.795	1.042	0.736	0.704	0.635
0.551	5.868	5.583	3.575	3.153	2.458
					2.451
0.796	7.742	8.254	4.130	3.840	3.302
					3.290
0.923	8.606	8.567	6.471	3.986	3.194
					3.378
1.69	12.64	13.39	7.571	5.093	4.844
1.97	15.21		9.376	5.299	5.283
2.46	14.35	15.54	9.853	5.380	
3.32	18.34	18.09	9.873	5.531	5.782
					5.704
3.56	19.09	17.60	10.60	5.508	5.571
5.01	18.72	18.14	11.16	5.015	5.318
					5.297
5.56		17.52	11.57	4.750	5.234
5.57	18.44	17.14	10.86	4.639	4.876
					5.130
6.74	17.82	17.26	10.97	4.635	4.841
	17.85				4.785

either the proton (H^+) or the undissociated acid (HA)[19 – 21], Eqs (*A*), (*B*). The existence of dimer of the catalyst acid is not likely in the medium studied by us[19 – 21].

$$\mathrm{T + H^+ \xrightarrow{\mathit{k}_H} P} \tag{A}$$

$$\mathrm{T + HA \xrightarrow{\mathit{k}_{HA}} P} \tag{B}$$

In the mechanism describing the specific acid catalysis, the protonated triazene is formed[14] and then decomposed into products in the rate-determining step (*C*).

$$\mathrm{T + H^+ \overset{\mathit{K}_{TH}}{\rightleftharpoons} TH^+ \xrightarrow{\mathit{k}'_H} P} \tag{C}$$

However, the schemes given cannot interpret the decrease in k_{obs} at higher concentrations of the catalyst acid. This decrease is probably caused by the decrease of concentration of reactive triazene in the reaction mixture due to formation of some less reactive complex involving the triazene molecule, e.g. a 1 : 1 (or 1 : 2) associate of the triazene with the undissociated acid[23]. Such complexes can be formed in fast pre-equilibria followed by very slow processes producing the products P (schemes (*D*), (*E*)).

$$\mathrm{T + HA \overset{\mathit{K}_{TK1}}{\rightleftharpoons} TK1 \xrightarrow{\mathit{k}'_{HA}} P} \tag{D}$$

$$\mathrm{TK1 + HA \overset{\mathit{K}_{TK2}}{\rightleftharpoons} TK2 \xrightarrow{\mathit{k}''_{HA}} P} \tag{E}$$

The associates of TK1 or TK2 types can be formed unless the catalyst acid is strong enough to transfer the proton to the substrate. The existence of the complexes of triazene with general acid was proved by measuring the observed rate constants of the decomposition of dicyclohexyl derivative at a constant proton concentration (c_{H^+} = 1.05 . 10^{-4} mol dm^{-3}) and variable concentration of undissociated acid (for c_{HA} = 0.061, 0.305, and 0.610 mol dm^{-3} it was k_{obs} = 3.038 . 10^{-3}, 2.458 . 10^{-3}, and 1.584 . 10^{-3} s^{-1}, respectively). The observed rate constants decrease with increasing concentration of pivalic acid and exhibit nearly the same decreasing trend as the k_{obs} values at higher concentrations of catalyst acid in the case of this substrate.

The analytical concentrations of acid and triazene in (*A*) – (*E*) and the corresponding equilibrium constants can then be expressed by Eqs (*1*) – (*6*).

$$c_{HA} = [H^+] + [HA] + [TK1] + [TK2] + [TH^+] \tag{1}$$

$$c_T = [T] + [TK1] + [TK2] + [TH^+] \tag{2}$$

$$K_{TK1} = [TK1]/[HA][T] \tag{3}$$

$$K_{TK2} = [TK2]/[HA][TK1] = [TK2]/K_{TK1}[HA]^2\,[T] \tag{4}$$

$$K_{TH} = [TH^+]/[T][H^+] \tag{5}$$

$$K_{HA} = [H^+][A^-]/[HA] = [H^+]^2/[HA] \tag{6}$$

Using Eqs (*1*) – (*5*) and the equation for the reaction rate one can suggest a summary relationship (*7*) for the dependence of observed rate constant upon the concentrations of catalyst pivalic acid and proton. When deriving this relationship we neglected, on the basis of the dissociation constant determined by us for pivalic acid in 40% ethanol ($K_{HA} = 1.8 \,.\, 10^{-7}$) and on the basis of the ratio of triazene to catalyst acid in the reac-

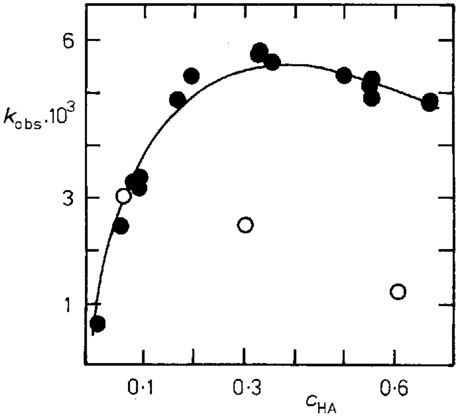


FIG. 1
Observed rate constants (k_{obs}, s^{-1}) of acid-catalyzed decomposition of 3,3-dicyclohexyl-1-phenyltriazene in 40 vol.% aqueous ethanol (empty circles correspond to samples titrated to proton concentration $c_{H^+} = 1.05 \,.\, 10^{-4}$ mol dm^{-3}; see Experimental). Curve represents dependence of k_{obs} vs catalyst acid concentration calculated according to Eq. (*10*)

tion medium, the concentrations of all the particles at the right-hand side of Eq. (*1*) except for [HA].

$$k_{\mathrm{obs}} = \frac{k''_{\mathrm{HA}}\,K_{\mathrm{TK2}}\,K_{\mathrm{TK1}}\,c^2_{\mathrm{HA}} + (k'_{\mathrm{HA}}\,K_{\mathrm{TK1}} + k_{\mathrm{HA}})c_{\mathrm{HA}} + (k'_{\mathrm{H}}\,K_{\mathrm{TH}} + k_{\mathrm{H}})[H^+]}{1 + K_{\mathrm{TK2}}\,K_{\mathrm{TK1}}\,c^2_{\mathrm{HA}} + K_{\mathrm{TK1}}\,c_{\mathrm{HA}} + K_{\mathrm{TH}}[H^+]} \qquad (7)$$

Using Eq. (*6*) and experimental dissociation constant of pivalic acid in the given medium (pK_{HA} = 6.74) one can write Eq. (*8*) for the proton concentration.

$$[\mathrm{H}^+] = 0.000424\,c^{1/2}_{\mathrm{HA}} \qquad (8)$$

The equation (*7*) obtained is relatively complex but provides the possibility of arranging a series of models with various powers of the concentration of catalyst acid both in the numerator and in the denominator. The various models were tested with the use of the data for the dicyclohexyl derivative which was measured in detail. For this derivative we also measured the decomposition k_{obs} values at the same proton concentration but various concentrations of the catalyst acid. The decrease in the observed rate constant with increasing concentration of the catalyst acid at the same proton concentration can be explained by the reaction course according to (*D*) and (*E*); in addition to it, the decrease indicates that in the final relationship there must be, side by side, a term containing the proton concentration and a term containing the acid concentration.

The decrease in k_{obs} at higher acid concentrations can be caused by the existence of the complexes TK1 or TK2 only if the complexes do not react further or react much more slowly than the other particles (i.e. $k'_{\mathrm{HA}} = k''_{\mathrm{HA}} = 0$). As a consequence, the reaction according to scheme (*B*) will not take place either, hence it is $k_{\mathrm{HA}} = 0$. On the basis of these facts, Eq. (*7*) can be simplified to Eq. (*9*).

$$k_{\mathrm{obs}} = k_{\mathrm{H}}[\mathrm{H}^+]/(1 + K_{\mathrm{TK2}}\,K_{\mathrm{TK1}}\,c^2_{\mathrm{HA}} + K_{\mathrm{TK1}}\,c_{\mathrm{HA}} + K_{\mathrm{TH}}[\mathrm{H}^+]) \qquad (9)$$

The solution of Eq. (*9*) by nonlinear regression (dicyclohexyl derivative: $s = 2.03 \cdot 10^{-4}$) gave the four parameters, out of which the K_{TK1} parameter was statistically insignificant ($t = 1.68$, $t_{\mathrm{crit}} = 2.10$) and the K_{TH} parameter was negative (without physical meaning) and, in addition to it, had the lowest *t* test value ($t = 0.18$). These results excluded the term containing the K_{TH} parameter, hence the mechanism of specific acid catalysis described in scheme (*C*) is not operating.

With regard to the lowered dimension of problem, the following calculations were carried for all the derivatives studied. In all the cases, the term involving the K_{TK1}

parameter turned out statistically insignificant (the results for the dicyclohexyl derivative are given as an example: $s = 2.21 \,.\, 10^{-4}$, $t(K_{TK1}) = 0.0$). The statistical insignificance of the term involving the K_{TK1} parameter indicates its negligible magnitude as compared with the other terms in the denominator as well as the validity of the inequality $K_{TK2} > K_{TK1}$. The resulting model can be expressed by Eq. (*10*) for the dicyclohexyl derivative (because Eq. (*8*) does not apply to solutions with the same proton concentration and different acid concentrations) or by simplified Eq. (*11*) for the other substrates:

$$k_{obs} \;=\; k_H[H^+]/(1 + K_K\, c_{HA}^2), \qquad (10)$$

$$k_{obs} \;=\; 0.000424\, k_H\, c_{HA}^{1/2}/(1 + K_K\, c_{HA}^2), \qquad (11)$$

where $K_K = K_{TK1}\, K_{TK2}$. The k_H, K_K values obtained for the dicyclohexyl derivative are identical whether or not the points obtained with the same proton and different acid concentrations have been involved in the calculations.

Table IV gives the calculated values of catalytic rate constant k_H and the stability constants K_K of the complex. Figure 1 presents the interpretation of the experimental dependence by a curve according to the model (*10*) for the dicyclohexyl derivative. The points denoted by empty circles represent the k_{obs} values for the titrated samples with the same proton concentration (see Experimental), the other points correspond to the values of Table III. Figure 1 represents only one section of the three-dimensional dependence of k_{obs} upon c_{HA} and $[H^+]$.

The catalytic rate constant k_H decreases with increasing size of alkyl, which unequivocally confirms the effect of substituents at N^3 atom upon the rate of acid catalyzed decomposition of 1-phenyl-3,3-dialkyltriazenes. The effect observed can be explained

TABLE IV
Optimized values of parameters in Eq. (*11*), their standard deviations and residual standard deviations *s*

R	k_H[a]	$s(k_H)$	K_K[b]	$s(K_K)$	$s \,.\, 10^3$	*n*
Me	77.35	3.87	1.02	0.248	1.38	13
Et	75.90	3.43	1.12	0.249	1.17	12
i-Pr	45.84	1.93	0.947	0.226	0.735	13
Bu	31.47	0.693	3.41	0.223	0.208	13
cHx[c]	28.17	0.597	2.30	0.157	0.235	22

[a] k_H, $dm^3\, mol^{-1}\, s^{-1}$; [b] K_K, $dm^6\, mol^{-2}$; [c] according to Eq. (*10*).

by hindered approach of solvated proton to the N^3 atom, which supports the statement of bimolecular reaction mechanism with general acid catalysis. The substituents at the N^3 atom could, however, simultaneously deform the triazene skeleton and thereby – on the other hand – increase its reactivity. In the final effect the steric effect of substituents can be a combination of both the influences discussed. In addition to it, at higher concentrations of acid the observed rate constant is diminished by the formation of the unreactive complexes TK1 and TK2. The combined stability constant K_K of these complexes has a higher value with the triazenes containing bulkier alkyl groups (butyl, cyclohexyl). Although the differences are not too high, the magnitude of stability constant of complex seems to be connected with the size of alkyl groups. The derivatives with bulkier alkyls probably undergo a deformation of triazene skeleton connected with lowering of conjugation between the free electron pairs at nitrogen atoms and the aromatic system of phenyl group. The thereby increased basicity of nitrogen atoms can facilitate the formation of the said complexes. Obviously, the hindered rotation (found with the dicyclohexyl and diisopropyl derivatives) has no effect on this process. The whole process is undoubtedly complicated by the participation of solvating molecules of water and ethanol. The unreactive complex TK not only makes the attack by the proton difficult, but the solvation of triazenes with water and ethanol molecules is made difficult too. Hence the steric effect is manifested in both the process (*A*) and, probably, the equilibrium (*E*), which indicates a relatively complex reaction course involving several equilibria not only between the reacting components but also with the participation of molecules of both solvents.

The kinetic data of Table III were also treated by the method of principal components[28] (PCA). The source matrix was arranged in such a way that the rows and columns corresponded to the individual substrates and the catalyst acid concentrations, respectively. This matrix was standardized before the calculation. The first three columns of the data matrix (i.e. the first three rows in Table III) were excluded from the calculation because of their lower modelling power. From the PCA method it follows that 98% of the variability is described by a single significant latent variable which is at the same time significant for all the columns. The concentrations participate uniformly in creating the model. As the score vector describes the quality of substrates, the latent variable is a new set of constants describing the substituent effects. In this case the dominant effect of substituents is their steric effect. The first principal component from the PCA calculation (PCA_1 : Me 3.39, Et 3.28, *i*-Pr –0.239, Bu –2.93, cHx –2.93) was used, in analogy to the classic steric constants[29] E_s and ν_{ef}, as the vector explaining the variables for the simple linear regression of the dependence of the catalytic rate constant k_H upon the steric parameters of the model substrates. Logically, the results of this calculation show that the effect of substituents is best described by the parameter obtained from the PCA calculation ($r = 0.995$). With the application of E_s parameters the correlation coefficient was $r = 0.908$, and with ν_{ef} the correlation was statistically insignificant. The correlation between the K_K values and the steric constants given was insignificant too. Hence the substituent effect on the course of the model reaction investigated is more complex and cannot be described by the substituent steric effects alone.

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