SUBSTITUENT EFFECTS IN HYDROLYSIS OF 3-CARBAMOYL-1,3-DIPHENYLTRIAZENES

Oldřich PYTELA, Miroslav VEČEŘA and Pavel VETEŠNÍK

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

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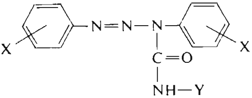
Fifteen substituted derivatives of 3-(N-methylcarbamoyl)-1,3-diphenyltriazene and nine substituted derivatives of 3-(N-phenylcarbamoyl)-1,3-diphenyltriazene have been synthetized. With 22 derivatives kinetic measurements have been carried out in acid, neutral and alkaline regions, and the respective catalytic constants have been determined. From the kinetic results the Hammett reaction constants have been calculated and used for discussion of the reaction mechanisms suggested earlier.

1,3-Diphenyltriazene derivatives of general formula



are described in literature predominantly from the synthetic viewpoint[1] connected with their commercial use[2-4]. The above compounds with Y = 4-Cl-C_6H_4, 3-Cl-C_6H_4, C_6H_5; X = H and Y = CH_3; X = 4-Cl were suggested as cancerostatics[2]. Patent literature[3] claims the derivatives with X = 4-CH_3O, 4-Cl; Y = CH_3 as pesticides. The urea derivative with Y = C_6H_5; X = H was applied as additive to polymers[4]. So far, however, literature gives no kinetic data concerning hydrolysis or another type of decomposition of the said derivatives. Our previous communication[5] dealt with kinetics and mechanism of hydrolysis of the unsubstituted 3-(N-methylcarbamoyl)-1,3-diphenyltriazene (*I*, Y = CH_3; X = H) and 3-(N-phenylcarbamoyl)-1,3-diphenyltriazene (*II*, Y = C_6H_5; X = H). The aim of the present communication is verification of our former mechanistic conclusions with the use of substituent effects.

EXPERIMENTAL

All the studied compounds were prepared by the described[5] methods. The reaction conditions, yields and physical properties are summarized in Table I. The numbers refer to the following X

TABLE I

The Solvents Used, Yields and Physical Properties of the Ureas *III* to *XXIV*

Compound	Solvent[a]	M.p., °C[b] yield, %	Formula m.wt.	Calculated/ /Found, % N
III	acetone	234 – 235 88·2	$C_{14}H_{12}N_6O_5$ 344·29	24·41 24·43
IV	acetone	191 – 194 81·7	$C_{14}H_{12}N_6O_5$ 344·29	24·41 24·80
V	acetone	229 – 232 86·1	$C_{16}H_{18}N_4O_5S_2$ 410·47	13·65 13·80
VI	acetone	224 – 226 86·2	$C_{16}H_{18}N_4O_5S_2$ 410·47	13·65 13·35
VII	acetone	233 – 236 81·3	$C_{16}H_{12}N_6O$ 304·31	27·62 27·80
VIII	acetone	105 – 108 81·3	$C_{16}H_{12}N_6O$ 304·31	27·62 27·25
IX	HA	107 – 110 89·4	$C_{14}H_{12}Cl_2N_4O$ 323·18	17·34 17·98
X	HA	69 – 72 91·7	$C_{14}H_{12}Cl_2N_4O$ 323·18	17·34 17·03
XI	HA	127 – 130 87·9	$C_{14}H_{12}Br_2N_4O$ 412·10	13·60 13·29
XII	HA	50 – 55 75·8	$C_{14}H_{12}Br_2N_4O$ 412·10	13·60 12·89
XIII	HA	85 – 90 80·3	$C_{14}H_{12}F_2N_4O$ 290·27	19·30 19·47
XIV	heptane	104 – 106 68·6	$C_{16}H_{18}N_4O$ 282·35	19·84 19·56
XV	heptane	116 – 118 47·3	$C_{16}H_{18}N_4O_3$ 314·35	17·82 18·00
XVI	acetone	185 – 195 82·9	$C_{18}H_{18}N_4O_3$ 338·37	16·56 16·76
XVII	acetone	127 – 129 78·1	$C_{19}H_{15}N_5O_3$ 361·36	19·38 19·01
XVIII	acetone	116 – 117 45·3	$C_{19}H_{15}N_5O_3$ 361·36	19·38 18·91
XIX	heptane	128 – 130 53·7	$C_{19}H_{15}ClN_4O$ 350·81	15·97 15·16

TABLE I
(*Continued*)

Compound	Solvent[a]	M.p., °C[b] yield, %	Formula m.wt.	Calculated/ /Found, % N
XX	heptane	104—105 48·3	$C_{19}H_{15}ClN_4O$ 350·81	15·97 15·55
XXI	heptane	127—128 63·8	$C_{20}H_{18}N_4O$ 330·39	16·96 17·21
XXII	heptane	110—111 58·3	$C_{20}H_{18}N_4O$ 330·39	16·96 17·31
XXIII	heptane	121—122 71·3	$C_{20}H_{18}N_4O_2$ 346·39	16·18 17·31
XXIV	heptane	101—103 68·7	$C_{20}H_{18}N_4O_2$ 346·39	16·18 17·23

[a] HA = heptane–acetone 1 : 1, [b] decomposition.

substituents (for Y = CH_3): *III* 4-NO_2, *IV* 3-NO_2, *V* 4-CH_3SO_2, *VI* 3-CH_3SO_2, *VII* 4-CN, *VIII* 3-CN, *IX* 4-Cl, *X* 3-Cl, *XI* 4-Br, *XII* 3-Br, *XIII* 3-F, *XIV* 4-CH_3, *XV* 4-CH_3O, *XVI* 4-CH_3CO, and to the following Y substituents (for X = H): *XVII* 4-NO_2-C_6H_4, *XVIII* 3-NO_2-C_6H_4, *XIX* 4-Cl-C_6H_4, *XX* 3-Cl-C_6H_4, *XXI* 4-CH_3-C_6H_4, *XXII* 3-CH_3-C_6H_4, *XXIII* 4-CH_3O-C_6H_4, *XXIV* 3-CH_3O-C_6H_4. The kinetic measurements were carried out in the described[5] way within the region of the last absorption band using the Specord UV VIS and VSU-2 apparatus (Zeiss, Jena). The experimental data were evaluated according to our optimization program[6] using an Odra 1013 computer. The pH values were determined with a PHM-4 apparatus (Radiometer, Copenhagen). The H_0 and H_- values were taken from refs[7,8]. The activation parameters were measured at pH 3·56 at at least five temperatures within 25·0°C to 55·0°C.

RESULTS AND DISCUSSION

The hydrolysis rate constants of the ureas *III*–*XXIV* were determined at various pH values to give the pH profiles. The experimental points were interlined by a curve which can be described by Eq. (*1*):

$$k_{\mathrm{obs}} = k_{\mathrm{H}}(a_{\mathrm{H^+}})^{\alpha} + k_0 + k_{\mathrm{OH}}(a_{\mathrm{OH^-}})^{\beta}/(K_{\mathrm{B}} + (a_{\mathrm{OH^-}})^{\beta}) \,. \qquad (1)$$

The symbols α and β are introduced to express the non-unity slopes of the acid and basic section, respectively, of the pH profile. From the experimental rate constants k_{obs} of the plateau we obtained the k_0 constants, and from the dependence log (k_{obs}

TABLE II

Hydrolysis Rate Constants of Disubstituted 3-(N-Methylcarbamoyl)-1,3-diphenyltriazenes *III* to *XVI* in Water at 25·0°C

Compound	k_0, s^{-1}	k_H, l mol^{-1} s^{-1}	α	k_{OH}/K_B l mol^{-1} s^{-1}	β
III	$1{\cdot}60 . 10^{-4}$[a]	—	—	—	—
IV	$1{\cdot}39 . 10^{-5}$	$1{\cdot}81 . 10^{-5}$	1·108[b]	$4{\cdot}86 . 10^{1}$	1·026
V	$1{\cdot}65 . 10^{-5}$[a]	—	—	—	—
VI	$1{\cdot}69 . 10^{-5}$	$5{\cdot}35 . 10^{-5}$	0·960	$2{\cdot}75 . 10^{0}$	0·939
VII	$4{\cdot}03 . 10^{-5}$	$5{\cdot}39 . 10^{-5}$	1·015	$5{\cdot}91 . 10^{1}$	1·023
VIII	$2{\cdot}11 . 10^{-5}$	$4{\cdot}11 . 10^{-5}$	1·089[b]	$4{\cdot}84 . 10^{0}$	1·088
IX	$1{\cdot}88 . 10^{-4}$	$5{\cdot}01 . 10^{-4}$	1·183[b]	$1{\cdot}93 . 10^{-2}$	1·036
X	$6{\cdot}89 . 10^{-5}$	$2{\cdot}49 . 10^{-4}$	1·045	$6{\cdot}74 . 10^{-2}$	0·679[b]
XI	$1{\cdot}12 . 10^{-4}$	$4{\cdot}87 . 10^{-4}$	1·091	$2{\cdot}39 . 10^{-2}$	0·801
XII	$8{\cdot}20 . 10^{-5}$	$1{\cdot}34 . 10^{-4}$	1·086	$6{\cdot}13 . 10^{-2}$	0·727[b]
XIII	$9{\cdot}57 . 10^{-5}$	$2{\cdot}67 . 10^{-4}$	1·099[b]	$9{\cdot}65 . 10^{-2}$	0·800[b]
XIV	$1{\cdot}01 . 10^{-3}$	$1{\cdot}45 . 10^{-2}$	0·886[b]	$8{\cdot}87 . 10^{-4}$	0·924
XV	$2{\cdot}63 . 10^{-3}$	$3{\cdot}67 . 10^{-2}$	0·895[b]	—	—
XVI	$2{\cdot}01 . 10^{-4}$	$1{\cdot}60 . 10^{-4}$	1·134[b]	$2{\cdot}00 . 10^{1}$	1·004

[a] Additionally calculated from the activation parameters; [b] statistically significant difference from unity at the significance level $\alpha = 0{\cdot}05$.

TABLE III

Hydrolysis Rate and Equilibrium Constants of Monosubstituted 3-(N-Phenylcarbamoyl)-1,3-diphenyltriazenes *XVII* to *XXIV* in Water at 25·0°C (Eq. (*1*), $\beta = 1$)

Compound	10^3k_0 s^{-1}	10^4k_H l mol^{-1} s^{-1}	α	k_{OH} s^{-1}	K_B mol l^{-1}
XVII	10·2	3·15	1·233	$1{\cdot}04 . 10^{1}$[a]	$2{\cdot}09 . 10^{-4}$[a]
XVIII	6·94	20·8	0·834[b]	$4{\cdot}17 . 10^{-2}$	$5{\cdot}99 . 10^{-3}$
XIX	3·93	20·5	0·782[b]	$1{\cdot}28 . 10^{-1}$	$1{\cdot}25 . 10^{-1}$
XX	4·77	7·67	0·963	$6{\cdot}54 . 10^{-2}$	$3{\cdot}70 . 10^{-2}$
XXI	2·55	18·6	0·931	$1{\cdot}79 . 10^{0}$[a]	$1{\cdot}07 . 10^{0}$[a]
XXII	2·32	15·5	0·526[b]	$9{\cdot}48 . 10^{-1}$[a]	$7{\cdot}87 . 10^{-1}$[a]
XXIII	2·01	27·2	0·749[b]	$3{\cdot}41 . 10^{0}$[a]	$2{\cdot}11 . 10^{0}$[a]
XXIV	3·64	25·3	0·892	$2{\cdot}21 . 10^{-1}$	$1{\cdot}51 . 10^{-1}$

[a] Additionally calculated from the Hammett relation (*8*); [b] statistically significant difference from unity at the significance level $\alpha = 0{\cdot}05$.

$- k_0)$ *vs* pH of the acid region we obtained the constants k_H and α by linear regression. The combined constant k_{OH}/K_B and the parameter β of the ureas *III*–*XVI* were determined by linear regression of the dependence $\log(k_{obs} - k_0)$ *vs* pOH, because here it is $K_B \gg a_{OH^-}$ up to pH ~ 15. The results are summarized in Table II. The constants K_B and k_{OH} could be isolated with the ureas *XVIII*, *XIX*, *XX* and *XXIV*. The constants determined in this way fulfil the Hammett relation (*8*), $r = 0.994$, which was used for assessment of K_B for *XVII*–*XXIV* (and also for assessment of k_{OH} from the combined constant k_{OH}/K_B). The results are given in Table III.

So far we have no explanation for the non-unity slopes. The situation where the slope is a fraction of or greater than unity (as it is the case with base-catalyzed hydrolysis of ureas[9,10]) can easily be explained by reaction of the substrate with several molecules of reagent. A variable slope smaller than unity was found by Mader[11] in alkaline hydrolysis of trifluoroacetanilide. The author explains it by simultaneous ionization of the substrate and reaction of its carbonyl group through the tetrahedral intermediate. However, the model necessitates simultaneous determination of eight constants. In literature there are also reports concerning the same substrate (4-nitrophenyl acetate) and giving (for the same pH range) variable slopes smaller than unity[12] or equal to unity[13].

Kinetic measurements of hydrolysis of some disubstituted derivatives in neutral medium gave the activation parameters summarized in Table IV. All the given results

TABLE IV

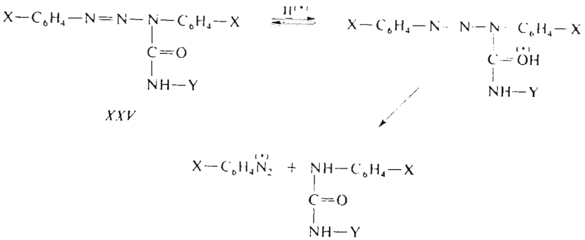
Activation Enthalpy $\Delta H^{\ddagger}$ and Activation Entropy $\Delta S^{\ddagger}$ of Hydrolysis of Disubstituted 3-(N-Methylcarbamoyl)-1,3-diphenyltriazenes *III* to *XIV* in Neutral Medium

Compound	X (Y = CH_3)	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J mol^{-1} K^{-1}
III	4-NO_2	90·76 ± 5·72	−14·70 ± 16·69
IV	3-NO_2	106·3 ± 4·4	17·03 ± 14·83
V	4-CH_3SO_2	131·8 ± 3·5	105·8 ± 12·8
VI	3-CH_3SO_2	93·97 ± 1·99	−15·17 ± 6·91
VII	4-CN	104·8 ± 1·4	23·45 ± 4·90
VIII	3-CN	101·4 ± 2·5	4·79 ± 8·67
IX	4-Cl	80·78 ± 4·48	−43·98 ± 16·30
X	3-Cl	98·21 ± 4·12	42·21 ± 14·50
XI	4-Br	87·64 ± 2·81	−24·55 ± 10·18
XII	3-Br	110·09 ± 3·25	40·65 ± 11·45
XIII	3-F	90·10 ± 9·85	−20·97 ± 34·63
XIV	4-CH_3	73·42 ± 2·56	−56·27 ± 9·36

were used in mechanistic discussion of the studied ureas in acid, neutral and alkaline regions.

The Hydrolysis in Acid Medium

In the previous communication[5] we suggested as the most favourable mechanism of the specific acid-catalyzed hydrolysis of the unsubstituted derivatives *I* and *II* that given in Scheme 1.



SCHEME 1

Substituent effects on acid hydrolysis of 3-(N-*methylcarbamoyl*)-1,3-*diphenyltriazenes* IV, VI *to* XVI. Relation between the found catalytic constants k_H (Table II) and the Hammett constants is given by Eq. (*2*):

$$\log k_H = -(3{\cdot}19 \pm 0{\cdot}16)\,\sigma - (2{\cdot}39 \pm 0{\cdot}07)\,, \quad r = 0{\cdot}987\,. \tag{2}$$

The reaction constant of acid-catalyzed hydrolysis of disubstituted 1,3-diphenyltriazenes is $\varrho = -5{\cdot}932$ (20°C, 20% aqueous ethanol)[14]. As the mechanisms are similar, the difference in the ϱ constants is due to different solvents and temperatures and obviously also to delocalization of positive charge (and hence to decreased sensitivity) in the ureas studied by us. The reaction constant is large in both the cases, which can be explained by superposition of two parallel influences (protonation and splitting off of the charged diazonium ion). Sign of the reaction constant also agrees with the suggested mechanism (Scheme 1).

Substituent effects on acid hydrolysis of monosubstituted 3-(N-*phenylcarbamoyl*)-1,3-*diphenyltriazenes* XVII–XXIV. Linear regression of the relation $\log k_H$ (Table III) *vs* σ constants gave Eq. (*3*):

$$\log k_H = -(0{\cdot}73 \pm 0{\cdot}14)\,\sigma - (2{\cdot}65 \pm 0{\cdot}05)\,, \quad r = 0{\cdot}903\,. \tag{3}$$

The low correlation coefficient is connected with the non-unity slope in the acid section of the pH profiles (the H_0 scale[7] was used, as H_A gave worse results). If compared with the reaction constants of acid-catalyzed hydrolysis of amides, the reaction constant found by us seems large and negative, especially so if the fact is taken into account that introduction of an imino group between carbonyl and aryl groups lowers sensitivity towards substitution by a factor of 2·2 (refs[15,16]). The reaction constants found with amides represent a superposition of two antagonistic influences – protonation of the amide group (ϱ_1: $-0{\cdot}933$, ref.[17]; $-1{\cdot}30$, ref.[18]; $-0{\cdot}48$, ref.[19]) and nucleophilic attack at the activated carbonyl (ϱ_2: 1·12 to 1·19, ref.[20]; 1·39 to 1·19, ref.[18]; 1·75, ref.[19]), hence the resulting reaction constant is small (ϱ: 0·19 to 0·26, ref.[20]; $-0{\cdot}11$ to 0·09, ref.[18]; 0·118, ref.[21]; $-0{\cdot}15$ (60% aqueous ethanol, 100°C), refs[22,23]). The given comparison supports the suggested hydrolysis mechanism of the studied ureas (Scheme 1), the common feature being only the first step (protonation).

The Hydrolysis in Neutral Medium

No suitable correlation analogs are given in literature for the non-catalyzed hydrolysis of the studied compound, two studies of hydrolysis of phenyl acetates[24,25] only being available so far (ϱ: 1·15 (60% aqueous acetone, 30°C); 1·16 (water, 30°C)). First of all, we followed the substituent effects on the non-catalyzed hydrolysis of disubstituted 3-(N-methylcarbamoyl)-1,3-diphenyltriazenes *III* to *XVI*. The dependence $\log k_0$ (Table II) *vs* the Hammett σ constants shows a break indicating two different mechanisms. The substrates carrying substituents with $\sigma \leqq 0{\cdot}7$ obey the relation (*4*), whereas for the derivatives *III*, *IV* and *VII* Eq. (*5*) is obeyed.

$$\log k_0 = -(2{\cdot}29 \pm 0{\cdot}07)\,\sigma - (3{\cdot}26 \pm 0{\cdot}03)\,, \quad r = 0{\cdot}996 \qquad (4)$$

$$\log k_0 = +(1{\cdot}95 \pm 0{\cdot}27)\,\sigma - (6{\cdot}26 \pm 0{\cdot}27)\,, \quad r = 0{\cdot}991^a \qquad (5)$$

In the first case we accept the mechanism suggested for the unsubstituted ureas *I* and *II* (Scheme 2) (ref.[5]), the formula *XXVI* denoting the hydrated complex ($Y = CH_3$).

In this mechanism effects of the same substituents in the two benzene rings are opposite. A substituent which facilitates the splitting off of the diazonium salt affects unfavourably the electron transfer from the split bond to the formed urea and *vice versa*. The Eq. (*4*) indicates a dominant effect of the substituent on electron stabilization of the formed diazonium cation. The substituents markedly retarding the diazonium salt formation (4-NO_2, 3-NO_2, 4-CN) cause obviously a change in the mechanism. The molecule is split between the N-methylcarbamoyl group and the triazene

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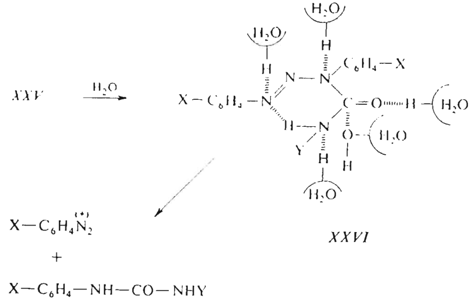
[a] For X = 4-NO_2 and 4-CN the σ^- constants were more suitable.

chain, which was confirmed by formation of 1,3-bis(4-nitrophenyl)triazene (which was proved chromatographically) as product of the non-catalyzed hydrolysis of the



SCHEME 2

nitro derivative *III*. In the Hammett equation (*5*) the exalted σ_p^- constants are more suitable, which agrees with the splitting mechanism of the respective N-methylcarbamoyltriazene to the triazene anion and methyl isocyanate or N-methylcarbamic acid, the latter substance being decomposed (at a rate depending on pH (ref.[25])) into methylamine and carbon dioxide. The whole process is given in Scheme 3 ($Y = CH_3$). The electron-acceptor substituents in the both rings have analogous stabilizing effect on the rate-limiting step of the described mechanism, which makes itself felt by a sign change of the reaction constant ($\varrho = 1{\cdot}95$).

$$\mathit{XXVI} \rightarrow X{-}C_6H_4{-}N{=}N{-}NH{-}C_6H_4{-}X + Y{-}NHCOOH$$

SCHEME 3

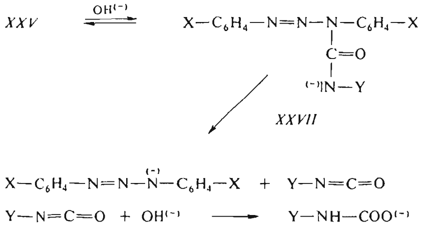
Substituent effects on non-catalyzed hydrolysis of the monosubstituted 3-(N-*phebylcarbamoyl*)-1,3-*diphenyltriazenes* XVII–XXIV. The Hammett equation has the form (*6*).

$$\log k_0 = (0{\cdot}62 \pm 0{\cdot}04)\,\sigma - (2{\cdot}54 \pm 0{\cdot}02)\,, \quad r = 0{\cdot}987\,. \qquad (6)$$

The magnitude and sign of the reaction constant agree with the distance between the substituent and the reaction centre and with character of the reaction centre in the above-suggested mechanism (Scheme 2, X = H; $Y = C_6H_4$—Z).

The Hydrolysis in Alkaline Medium

The investigation of the non-substituted ureas *I* and *II* indicates the ElcB mechanism type to be the most likely in the base-catalyzed hydrolysis (Scheme 4, X = H, Y = CH_3 and C_6H_5).



SCHEME 4

Substitutent effects on specific base-catalyzed hydrolysis of 3-(N-methylcarbamoyl)-1,3-diphenyltriazenes *IV*, *VI* to *XVI* are expressed by the Hammett equation (7):

$$\log k_{OH}/K_B = (4{\cdot}34 \pm 0{\cdot}27)\,\sigma - (2{\cdot}50 \pm 0{\cdot}14)\,, \quad r = 0{\cdot}983^a\,. \tag{7}$$

This result agrees with the reaction constants found with the reactions which evidently proceed by the ElcB mechanism and show a great substituent sensitivity (ϱ: phenyl N-methylcarbamates +3·17 (20% aqueous dioxane, 25°C) (ref.[15]); +2·34 (water, 25·0°C) (ref.[26]); +2·80 (water, 25°C) (ref.[27])). The alternative mechanism $B_{Ac}2$ (in the case of the studied substrates see Scheme 5), on the contrary, shows a low substituent sensitivity (ϱ: phenyl acetates +1·1 (water, 30°C) (ref.[28]); substituted phenyl benzoates +1·28 (water–acetonitrile 2 : 1, 25°C) (ref.[29]); phenyl acetates +1·0 (28% aqueous ethanol, 30°C) (ref.[24]); phenyl N,N-dimethylcarbamates +1·00 (water, 25°C) (ref.[30])). As our ϱ value is at least 2·168 (related to one substituent, regardless of different transfers), the found relation confirms the formerly suggested mechanism (Scheme 4, Y = CH_3). Dependence of logarithm of the catalytic rate constant (Table II) on pK value of the leaving group[14] gives the Brönsted constant $\beta = -1{\cdot}62$. In accordance with the discussion presented by Williams[31] a high β value is characteristical for the ElcB mechanism (Scheme 4). The alkaline hydrolysis products of some disubstituted 3-(N-methylcarbamoyl)-1,3-diphenyltriazenes (X = 3-NO_2,

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[a] For X = 4-CN and 4-CH_3CO the σ^- constants were more suitable.

4-CN, 4-Cl, 4-Br, 3-Br) showed a decreased solubility in the reaction medium. In the case of the urea *IX* (X = 4-Cl) the product was isolated and identified as the expected reaction product (*i.e.* 1,3-bis(4-chlorophenyl)triazene) by means of its melting point, ^{1}H-NMR spectra and TL chromatography on Silufol. The decreased solubility of diphenyltriazenes is explained by association of the molecules[32]. Hunter[33] presumes formation of dimers and even polymers with water and another oxygen-containing solvent.

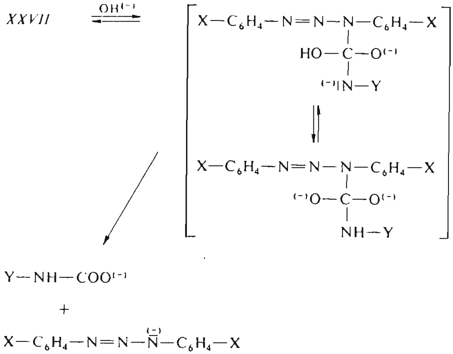
Furthermore, we followed the substituent effect on the base-catalyzed hydrolysis of the monosubstituted 3-(N-phenylcarbamoyl)-1,3-diphenyltriazenes *XVII*–*XXIV*. Other substituent effects than those of the substituents in the leaving group were studied to a lesser extent in the context of mechanism of the base-catalyzed hydrolysis. The most frequent are the studies in the field of esters (*e.g.* substituted phenyl benzoates XC_6H_4COOPh, $\varrho = 1{\cdot}982$ (water–acetonitrile 2 : 1, 25°C) (ref.[29])). For benzamide it was found[22] $\varrho = 0{\cdot}7$ (60% aqueous ethanol, 100°C), for phenyl N-subst. phenylcarbamates it was found[15] $\varrho = 0{\cdot}64$ (20% aqueous dioxane, 25°C). The K_B and k_{OH} values (Table III) were plotted against the Hammett σ constants to give Eqs (*8*) and (*9*), respectively, the former relating to only *XVIII*, *XIX*, *XX*, *XXIV* and the latter relating to all derivatives except for *XVII* and *XVIII*.

$$\log K_B = -(2{\cdot}67 \pm 0{\cdot}23)\,\sigma - (0{\cdot}37 \pm 0{\cdot}03)\,, \quad r = 0{\cdot}994\,, \tag{8}$$

$$\log k_{OH} = -(2{\cdot}75 \pm 0{\cdot}49)\,\sigma - (0{\cdot}20 \pm 0{\cdot}17)\,, \quad r = 0{\cdot}982\,. \tag{9}$$

The ϱ constant found for the equilibrium constants K_B shows reasonable agreement with that found for dissociation of phenols to phenolates ($\varrho = -2{\cdot}113$), which allows to postulate a possibility of ionization at nitrogen of the carbamoyl group of the substrates. The dependence log k_{OH} *vs* σ is divided into two parts belonging probably to different mechanisms. In the case described by Eq. (*9*) we presume the mechanism given in Scheme 4 (X = H, Y = C_6H_4—Z). If the rate-limiting step consists in splitting of a bond to a not very good leaving group (pK = 13·27, 20% aqueous ethanol, 20°C) (ref.[14,34]), then the found reaction constant agrees with the expected one. A quite opposite situation is encountered with the nitro derivative *XVII*. On the basis of extrapolation from Eq. (*8*) it can be expected that the proton at the nitrogen atom of the carbamoyl group will show an enhanced ability to be split off. On the contrary, the discussed substituent hinders the electron-trasfer to the leaving group and formation of the respective phenyl isocyanate. The second effect is obviously dominant, and the decomposition does not take place until after the attack of the conjugated base of the substrate by another hydroxyl ion (analog of $B_{Ac}2$). The whole process can be described by Scheme 5 (X = H, Y = C_6H_4—NO_2). The difficult attack of the ionized substrate by the anion explains the high positive slope ($\varrho \approx 4{\cdot}5$). Among the products of the base-catalyzed hydrolysis of urea *XVII* we could find

1,3-diphenyltriazene and 4-nitroaniline, which agrees with the suggested mechanism (Scheme 5).



SCHEME 5

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