

KINETICS OF SPLITTING AND DEPROTONATION EQUILIBRIA OF MONOSUBSTITUTED AND SYMMETRICALLY DISUBSTITUTED DIARYLTRIAZENES

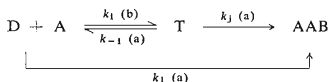
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Decomposition of monosubstituted and symmetrically disubstituted 1,3-diphenyltriazenes has been studied. The investigated compounds in acid medium undergo protonation followed by rapid decomposition to diazonium salt and amine. In alkaline solutions reversible hydrolytic splitting off of the proton takes place, the anions formed remaining undecomposed. Dissociation constants of the studied compounds have been determined in alkaline medium, and apparent rate constants of their decomposition have been determined in acid medium. All the values found fit the Hammett relation in the Yukawa-Tsuno modification.

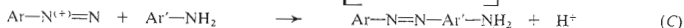
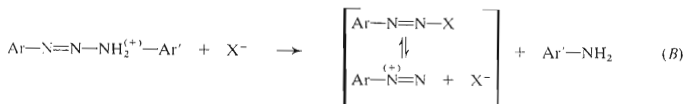
Reactions of diazonium salts with amines give various products according to the reaction medium used. In literature it is stated generally that in alkaline or very slightly acidic media the reaction produces the triazene (diazoamino compound), whereas in strongly acidic medium the aminoazo compound is formed which can also be the product of the acid-catalyzed rearrangement of the triazene. The mentioned reactions are summarized in Scheme 1, where D, A, T and AAB stand for diazonium salt, amine, triazene and aminoazobenzene, respectively, (a) means strongly acidic and (b) basic or slightly acidic media, and k 's are the corresponding rate constants.



SCHEME 1

If only the end products of the individual steps are considered, the given Scheme is exhausting. From the kinetical viewpoint, however, confusion arises in the case of reactions of diazonium salts with amines in acidic medium, where magnitudes and mutual ratios of the individual rate constants are significant. The reaction characterized by the constant k_1 — C-coupling of diazonium salts with amines in strongly acidic medium — is well known and described by many authors (we dealt with it in one of our previous papers¹, too). Not quite clear in this respect appear the remaining reaction steps involving triazene as the key compound.

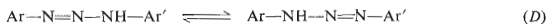
According to Griess and Martius² triazene is transformed into aminoazo compound in prototropic medium. Frieswell and Green^{3,4} presumed that the reaction goes through two steps: splitting of triazene into amine and diazonium ion, and subsequent azo coupling at carbon atom. The first experimental evidence for this intermolecular rearrangement was found by Nietzki⁵. The reaction was followed in decomposition of (4,4'-dimethyl)-1,3-diphenyltriazenes in the presence of aniline hydrochloride and *o*-toluidine hydrochloride. Formation of diazonium ion during the reaction was proved by Suizu and Yokozima⁶. It is stated⁷ that the reaction carried out in this way is catalyzed not only by acid, but it is accelerated also by the presence of the amine hydrochloride. At present, the mechanism by Hughes and Ingold^{8,9} is generally accepted (Scheme 2).



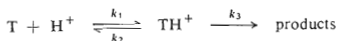
Ar = aryl

SCHEME 2

If the reaction involves diazonium ion in the step (B), it must be expected to be a second order reaction. Intermediary formation of $\text{Ar}-\text{N}=\text{N}-\text{X}$ depends also on concentration of X^- , and the reaction is then of the third order. In each case, however, the reaction involves the pre-equilibrium (A) which can (in the case of unsymmetrically substituted triazene) be complicated by the tautomeric equilibrium (D).



In literature there are not enough experimental data for kinetic study of decomposition of aromatic triazenes. The only authors who dealt with this problem from the kinetical viewpoint were Kruglov, Ershov and Charcharov¹⁰. They investigated decomposition of substituted bis-hydroxyethylphenyltriazenes and used the basic relation of pseudomonomolecular reaction for interpretation of their results, not regarding the rapid protonation pre-equilibrium. They also tried to evaluate the substituent effect on the decomposition rate ($\rho = -4.0$, $t = 40^\circ\text{C}$). In the case of aliphatic-aromatic triazenes the system is simplified by the absence of tautomeric equilibrium. The reaction system of aromatic triazenes can be solved with the use of the steady state treatment giving the kinetic equation of the summary decomposition of triazene in acid medium. (The triazene T in the suggested Scheme 3 involves, of course, the both tautomeric forms).



SCHEME 3

Suppose that $k_1 \gg k_3$, we obtain a simplified expression for the decomposition rate of triazene (Eq. (I)) integration of which gives Eq. (2) where $k' = (k_3/K_a) [H^+]$.

$$-d[T]/dt = (k_1 k_3/k_2) [H^+] [T] \quad (1)$$

$$k't = \ln ([T]_0/[T]_t) \quad (2)$$

This expression for observed rate constant k' should enable the determination of the resultant rate constant of the summary decomposition (provided K_a is known) which is identical with the constant k_3 of the slowest, rate-determining, reaction step.

The aim of this work is a study of the accessible properties of mono- and disubstituted 1,3-diphenyltriazenes and of their decomposition kinetics in acid medium.

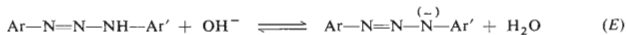
EXPERIMENTAL

Reagents

Asymmetrically and most symmetrically substituted 1,3-diphenyltriazenes (substituents in 3 or 4 position) were synthesized by two methods according to the type of substituent. The first one (a) for the compounds with electron-donor substituents¹¹ and the second one (b) for those with electron-acceptor substituents¹². Some symmetrically substituted triazenes (*m*-Br, *m*-CN, *p*-F, *p*-CH₃) were synthesized by a different method¹³ (c) (Table I). The triazenes were purified by crystallization from various solvents, chromatography on an alumina column or on non-impregnated W-3 paper. Mixtures of disodium hydrogen phosphate and citric acid in various proportions¹⁴ were used as buffers for kinetic measurements. Ionic strength was adjusted by addition of potassium chloride. All the reagents used were commercial chemicals of *p.a.* purity grade.

Ionisation Constants

a) *Splitting off of the proton in alkaline medium* (Eq. (E)), where the triazenes are completely stable, was followed spectrophotometrically¹⁵ at $20 \pm 0.1^\circ\text{C}$ in concentrations of 10^{-4} mol/l.



The used medium was 20% ethanolic sodium hydroxide or buffers according to Sørensen and Walbum¹⁶ (borax, sodium hydroxide). Ionic strength was not corrected. The analytical wavelengths were determined with a Unicam SP 800 B spectrophotometer, and precise absorbance measurements were carried out with a Zeiss VSU-2 apparatus; pH of the solutions measured was determined with a PHM apparatus (Radiometer Copenhagen) using a standard calomel electrode and a glass electrode G 200 B. The pH meter was calibrated with standard borax buffer pH 9.22. Results of the measurements are summarized in Table I.

b) *Addition of the proton* (Eq. (F)). Neither spectrophotometric nor titration determination of ionisation constants of this process was possible, as the subsequent decomposition was very rapid.



TABLE I

List of the Used Substituted Diphenyltriazenes, their Preparation Methods, (*a*, *b*, *c*) pK_a Values, and Decomposition Rates in 20% (by vol.) Ethanol at 20°C at *I* 0.5

Substituent	Method	pK_a	$\log k_3 + pK_a$
4-OCH ₃	<i>a</i>	—	5.33 ± 0.04
4-CH ₃	<i>a</i>	13.35 ± 0.05	4.95 ± 0.03
3-CH ₃	<i>a</i>	—	4.59 ± 0.04
H	<i>a</i>	13.26 ± 0.04	4.55 ± 0.02
4-F	<i>b</i>	—	4.51 ± 0.03
4-Cl	<i>b</i>	12.75 ± 0.03	3.98 ± 0.05
4-Br	<i>b</i>	12.75 ± 0.04	3.87 ± 0.02
4-COOCH ₃	<i>b</i>	—	2.91 ± 0.02
3-F	<i>b</i>	12.60 ± 0.01	3.65 ± 0.02
3-COCH ₃	<i>b</i>	12.62 ± 0.03	3.61 ± 0.05
3-COOCH ₃	<i>b</i>	—	3.59 ± 0.03
3-Br	<i>b</i>	12.53 ± 0.03	3.52 ± 0.03
3-Cl	<i>b</i>	12.50 ± 0.03	3.57 ± 0.03
4-COCH ₃	<i>b</i>	12.16 ± 0.03	2.77 ± 0.03
3-CN	<i>b</i>	12.27 ± 0.03	2.92 ± 0.02
4-CN	<i>b</i>	11.63 ± 0.05	2.38 ± 0.01
3-NO ₂	<i>b</i>	11.99 ± 0.04	2.71 ± 0.02
4-SO ₂ CH ₃	<i>b</i>	11.95 ± 0.04	2.19 ± 0.02
4-NO ₂	<i>b</i>	11.28 ± 0.03	1.57 ± 0.02
3-SO ₂ CH ₃	<i>b</i>	12.15 ± 0.02	—
3,3'-(NO ₂) ₂	<i>b</i>	10.90 ± 0.04	0.87 ± 0.05
4,4'-(NO ₂) ₂	<i>b</i>	9.90 ± 0.04	-0.32 ± 0.01
3,3'-(SO ₂ CH ₃) ₂	<i>b</i>	10.98 ± 0.02	1.06 ± 0.06
3,3'-(F) ₂	<i>b</i>	—	3.02 ± 0.02
4,4'-(F) ₂	<i>c</i>	12.95 ± 0.01	5.10 ± 0.04
3,3'-(Cl) ₂	<i>b</i>	12.23 ± 0.03	2.88 ± 0.03
4,4'-(Cl) ₂	<i>b</i>	—	3.78 ± 0.02
3,3'-(CN) ₂	<i>c</i>	11.29 ± 0.03	1.46 ± 0.08
4,4'-(CN) ₂	<i>b</i>	10.78 ± 0.03	0.48 ± 0.04
3,3'-(Br) ₂	<i>c</i>	12.28 ± 0.03	2.96 ± 0.01
4,4'-(Br) ₂	<i>b</i>	12.68 ± 0.03	3.49 ± 0.02
4,4'-(OCH ₃) ₂	<i>b</i>	—	6.66 ± 0.03
4,4'-(CH ₃) ₂	<i>c</i>	—	5.70 ± 0.04
4,4'-(COCH ₃) ₂	<i>c</i>	11.09 ± 0.02	1.40 ± 0.05
4,4'-(SO ₂ CH ₃) ₂	<i>b</i>	10.53 ± 0.03	0.03 ± 0.03

Kinetic Measurements

Kinetic measurements of decomposition of asymmetrically or symmetrically 3- and 4-substituted 1,3-diphenyltriazenes were carried out by spectrophotometric continuous following the triazene decrease with time. The reaction took place in phosphate buffer in 20% (by vol.) aqueous ethanol at 20°C at the ionic strength 0.5. In a 25 ml calibrated flask the triazene was dissolved in ethanol, the concentration being of the order 10^{-4} mol/l. The proper measurements were carried out with the Unicam SP 800 apparatus. In a 3 cm cell 9 ml buffer was pipetted and 1 ml alcoholic triazene solution was added from a syringe. In this way spectra of the triazenes were measured at higher pH values where decomposition did not interfere. The wavelength of the absorption maximum of the triazene read from its spectrum was adjusted in the apparatus, and time changes of the triazene absorbance due to decomposition were followed. The time course of the whole spectrum was also followed which confirmed that absorption maxima were not shifted during the reaction. pH of the reaction mixture was measured with the Radiometer Copenhagen PHM-4c apparatus.

Influence of the buffer concentration on the triazene decomposition was followed by changing the concentration of acetic acid and sodium acetate¹⁴ at constant ionic strength ($I = 0.5$), the same procedure was used also for the buffer composed of $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$ and citric acid.

Influence of ionic strength on the triazene decomposition was followed in a series of phosphate buffers with constant pH and various ionic strength (addition of KCl). The results are summarized in Table I and Figs 1–4.

RESULTS AND DISCUSSION

Overall triazene decomposition in acid medium can be described by Scheme 3. The steady state approximation gives the expression for the observed rate constant k' of pseudomonomolecular 1. order decomposition (Eq. (3)), where $k' = (k_3/K_a) [\text{H}^+]$.

$$-d[\text{T}]/dt = k'[\text{T}]. \quad (3)$$

With respect to that it is impossible to determine concentration of the protonated form of triazene due to its very rapid decomposition, it is impossible to determine the ionisation constants by available methods. The ionisation constant must be known for calculation of the thermodynamic rate constant of the decomposition. The rate constants of triazene decomposition measured by us represent, in fact, the decomposition rate constants divided by the ionisation constants. Logarithmic form of Eq. (3) is given in Eq. (4). The values of k_3 and $\text{p}K_a$ were measured and calculated for

$$\log k_3 + \text{p}K_a = \log k' + \text{pH} \quad (4)$$

the overall decomposition of nineteen *m*- and *p*-monosubstituted 1,3-diphenyltriazenes, and their dependence on the Hammett σ constants was investigated (Fig. 1). The experimental results turned out to fit the Yukawa–Tsunoo modification¹⁷ of the Hammett equation in the form (5).

$$\log k_3 + \text{p}K_a = \log k_3^0 + \text{p}K_a^0 + \rho(\sigma + r(\sigma_p^- - \sigma_p)). \quad (5)$$

Double regression¹⁸ gave parameters of this equation: $\log k_3^0 + pK_a^0 = 4.54$, $\rho = 2.59$, and $r = 0.66$; the overall correlation coefficient $R = 0.992$, standard deviation $s_3 = 0.02$. However, in fact this equation is a sum of relations for the reaction rate and for dissociation (Eqs (6) and (7), respectively),

$$\log k_3 = \log k_3^0 + \rho_K \sigma, \quad (6)$$

$$pK_a = pK_a^0 + \rho_D \sigma, \quad (7)$$

where ρ_K and ρ_D are the reaction constants for the reaction rate and for dissociation, respectively. Thus ρ in Eq. (5) is a sum of these two reaction constants. With respect to tautomerism it is obvious that even this resultant reaction constant involves two dissociation processes of the two possible tautomeric forms of the compounds studied, and it expresses rates of two tautomers.

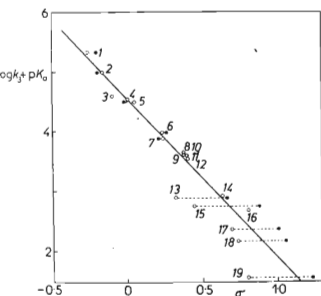


FIG. 1

Correlation of the Quotient of Decomposition Rate Constant and Dissociation Constant of 3- or 4-Substituted Diphenyltriazenes with the Hammett σ Constants (20% by vol. aqueous ethanol, 20°C, 1:0.5)

1 4-OCH₃, 2 4-CH₃, 3 3-CH₃, 4 H, 5 4-F, 6 4-Cl, 7 4-Br, 8 3-F, 9 3-COCH₃, 10 3-COOCH₃, 11 3-Cl, 12 3-Br, 13 4-COOCH₃, 14 3-CN, 15 4-COCH₃, 16 3-NO₂, 17 4-CN, 18 4-SO₂CH₃, 19 4-NO₂

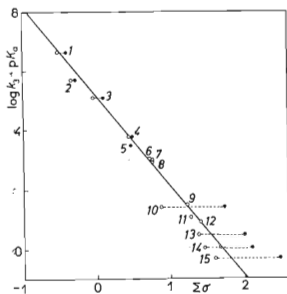


FIG. 2

Correlation of the Quotient of Decomposition Rate Constant and Dissociation Constant of Symmetrically Disubstituted Diphenyltriazenes with the Hammett σ Constants (20% by vol. aqueous ethanol, 20°C, 1:0.5)

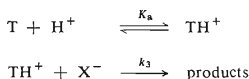
1 4,4'-(OCH₃)₂, 2 4,4'-(CH₃)₂, 3 4,4'-(F)₂, 4 4,4'-(Cl)₂, 5 4,4'-(Br)₂, 6 3,3'-(F)₂, 7 3,3'-(Br)₂, 8 3,3'-(Cl)₂, 9 3,3'-(CN)₂, 10 4,4'-(COCH₃)₂, 11 3,3'-(SO₂CH₃)₂, 12 3,3'-(NO₂)₂, 13 4,4'-(CN)₂, 14 4,4'-(SO₂CH₃)₂, 15 4,4'-(NO₂)₂.

We tried to exclude the effect of tautomerism by measuring the decompositions of fifteen 3,3'- or 4,4'-disubstituted 1,3-diphenyltriazenes. The values found were evaluated as in the previous case. Again the experimental results agreed with the Yukawa-Tsuno modification of the Hammett equation (Eq. (8), Fig. 2).

$$\log k_3 + pK_a = 5.078 - 2.966(\sigma + 0.311(\sigma_p^- - \sigma_p)); R_3 = 0.996 \quad (8)$$

From the both dependences it follows that ρ_K and ρ_D have the same sign, *i.e.* with increasing electron-acceptor character of the substituents the both basicity and decomposition rate of the triazenes decrease, the substituents with resonance effect being more efficient than those with predominant inductive effect.

In the case of the decomposition of 3,3'-difluoro-1,3-diphenyltriazene we tried to find whether or not the reaction rate depends on concentration of base. If Scheme 4



SCHEME 4

is considered, then the decomposition mechanism can be represented by a kinetic equation in which the observed rate constant k' is given by Eq. (9).

$$k' = (k_3/K_a) [H^+] [X^-]. \quad (9)$$

From the expression for k' it is seen that the rate constant should increase with increasing base concentration in this case. However, in our case the observed rate constant k' was the same at various concentrations of both acetate and phosphate buffers. It means that in the studied range the anion concentration does not affect the reaction rate, and the reaction is not subject to general base catalysis.

This result was confirmed also by the study of dependence of the decomposition rate of the triazenes on ionic strength. Dependence of the rate constant k' on ionic strength in diluted solutions is given by Eq. (10), where S is a constant depending on the dielectric constant of the medium, and Z_A, Z_B stand for charges of the reacting

$$\log k' = \log k'_0 + 2SZ_AZ_B\sqrt{J} \quad (10)$$

ions. If Scheme 4 is considered, then the pre-equilibrium involves a reaction of a charged particle with neutral molecule, *i.e.* ionic strength should have no effect on the reaction rate. In the case of the base-catalyzed reaction two charged species react, and ionic strength should affect the reaction rate (negative salt effect¹⁹).

From our study of the dependence of the reaction rate on ionic strength it follows, however, that the change of ionic strength (up to 1 mol) does not affect the magnitude of the rate constant, *i.e.* the reaction takes place between one charged species and one neutral molecule, and no general base catalysis is operating.

Dependence of pK_a (splitting off of the proton from the monosubstituted triazenes) on the substituent constants again fits the Yukawa-Tsuno modification¹⁷ of the Hammett equation (Fig. 3, Eq. (11)).

$$pK_a = 13.12 + 1.52(\sigma + 0.97(\sigma_p^- - \sigma_p)); \quad R = 0.975; \quad n = 15. \quad (11)$$

Analogous situation is encountered with the symmetrically disubstituted triazenes, too, (Fig. 4, Eq. (12)).

$$pK_a = 13.30 + 1.63(\sigma + 0.78(\sigma_p^- - \sigma_p)); \quad R = 0.985; \quad n = 12. \quad (12)$$

Comparison of the two dependences indicates (especially with regard to the magnitude of the correlation coefficients) that the both relations are practically equally significant. Therefrom it can be deduced that in the monosubstituted series tautomerism plays no important role (in the disubstituted series tautomerism is excluded).

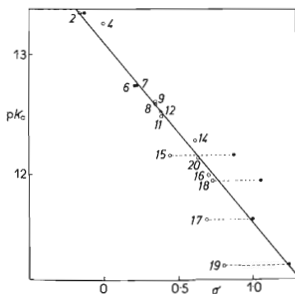


FIG. 3

Dependence of pK_a Values of Monosubstituted Diphenyltriazenes on the Hammett Substitution Constants

For description of points see Fig. 1.

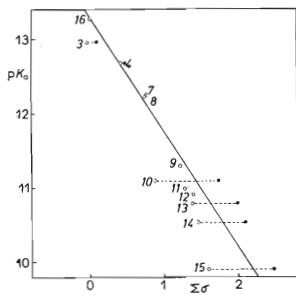


FIG. 4

Dependence of pK_a Values of Symmetrically Disubstituted Diphenyltriazenes on the Hammett Substitution Constants

For description of points see Fig. 2.

In one tautomeric form of the monosubstituted triazenes the substituent influences the reaction centre directly (as in aniline), the reaction constant being *e.g.* ρ_1 . In the other tautomeric form its action is weakened by the inserted azo group $-\text{N}=\text{N}-$ (the reaction constant *e.g.* ρ_2). Measurements of other compounds series showed²⁰ that azo group lowers the reaction constant value to 10–30% of the original value. If this presumption were valid in the series of tautomeric monosubstituted triazenes, then the dependence of ionisation constants would not be linear, but it would decrease more and more steeply with increasing electronegativity of substituents. Hence, either the presumption ρ_1/ρ_2 is not valid here or the shift of the tautomeric equilibrium is negligible (or combination of the both possibilities).

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