

Mechanism of acid-catalysed decomposition of 3-alkyl-1,3-diphenyltriazenes by trichloroacetic acid in hexane

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ABSTRACT: Eight 3-alkyl-1,3-diaryltriazenes with methyl, ethyl, propyl, butyl, pentyl, isopropyl, *sec*-butyl and cyclohexyl substituents were synthesized and their rate constants of decomposition by trichloroacetic acid (0.01–0.25 mol dm^{−3}) in hexane at 25 °C were measured. The kinetic model and mechanism thereof were studied by modelling of the dependences of k_{obs} on the concentration of trichloroacetic acid. On the basis of this kinetic model and the interpretation of solvent effects, a reaction mechanism was suggested according to which the triazene reacts with monomer and obviously also opens the dimer of trichloroacetic acid in a single reaction step. At the same time, a non-reactive associate between the N1 nitrogen of triazene and two molecules of trichloroacetic acid is formed in the reaction mixture. The equilibrium and rate constants depend on the addition of trichloroacetic acid as the co-solvent. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: triazenes; acid catalysis; kinetic model; mechanism

INTRODUCTION

Studies on reactivity of triazene derivatives have so far been focused especially on the kinetics and mechanism of acid-catalysed splitting of the triazene chain. Earlier workers preferred a mechanism of specific catalysis which involves decomposition of 1,3-diaryltriazene protonated at the N3 atom in the rate-limiting step,^{1–3} and the same conclusions were drawn for 1,3-dialkyltriazenes and 1,3,3-trialkyltriazenes.^{4,5} However, a number of other papers give arguments supporting the mechanism of general acid catalysis for both 1,3,3-trialkyltriazenes⁶ and 3-alkyl-1-aryltriazenes.^{7–11} General acid catalysis was demonstrated by studies of substitution effects in the acid-catalysed decomposition of 1-aryl-3-methyl-3-phenyltriazenes,¹² in the reaction of 3-methyl-1,3-diphenyltriazene with chloroacetic, formic and succinic acids in 40% aqueous ethanol¹³ and was indicated in a study of the acid-catalysed decomposition of 1,3-bis(4-methylphenyl)triazene in alcohols,¹⁴ aprotic solvents¹⁵ and water–methanol mixtures of various methanol concentrations.¹⁶ The participation of general acid catalysis was also proven in the thermal *cis*–*trans* isomerization of 1,3-diphenyl-

triazene in an aqueous medium. The N3 atom of 1,3-diphenyltriazene was estimated to be only a very weak base,¹⁷ and the existence of a stable substrate protonated at this centre in a specific acid catalysis is highly unlikely. Quantum-chemical calculations on triazene, on both *ab initio*^{18,19} and PM3 semiempirical bases,²⁰ indicated that the protonation of triazene can take place at both the N1 and N3 atoms. 1,3-Diphenyltriazene protonated at the N3 nitrogen atom exhibits a weakening of the N2–N3 bond (lengthened by about 0.2 Å), while the decomposition products (i.e. the diazonium salt and aniline) become more stable thermodynamically.²⁰ Therefore, it can be deduced that the protonated intermediate would rapidly decompose to products if it were formed.

The physico-chemical properties and reactivity of 3-alkyl derivatives of 1,3-diphenyltriazene with acids have received little attention thus far: only the 3-methyl derivative has been described.^{12,13,21–23} This is surprising since 3-alkyl-1,3-diphenyltriazenes are suitable substrates for verification of mechanisms of acid catalysis: in addition to the inductive effect, steric effects can also participate here. Another advantage is that the reaction can be studied in a wide variety of solvents, including aprotic types.

The aim of this work was to study these substituent effects for the purpose of verification of the mechanism of acid catalysis in the acid-catalysed decomposition of 3-alkyl-1,3-diphenyltriazenes. For this purpose we chose kinetic monitoring of the reactions of these compounds with trichloroacetic acid (a bulky general acid) of varying concentration in an inert medium of hexane.

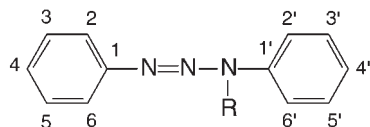
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EXPERIMENTAL

Synthesis of 3-alkyl-1,3-diphenyltriazenes. The 3-alkyl-1,3-diphenyltriazenes of the general formula shown were synthesized by azo coupling of a benzenediazonium salt with the respective *N*-alkylanilines.¹² Because of their thermal instability,²⁴ the products obtained were purified by column chromatography on alumina with tetrachloromethane as the mobile phase. Except for the solid methyl derivative (m.p. 34–34.5 °C), they are orange oils. The identities of the compounds prepared were checked by ¹H and ¹³C NMR spectroscopy (*N*-alkylanilines in CDCl₃, 3-alkyl-1,3-diphenyltriazenes in DMSO-*d*₆, Bruker AMX 360 spectrometer).



3-Methyl-1,3-diphenyltriazene. Yield 76%. ¹H NMR (DMSO-*d*₆), δ 7.19, 1H, (H-4'); 7.31, 1H (H-4); 7.43–7.51, 4H (H-3,5 and H-3',5'); 7.56–7.62, 4H (H-2,6 and H-2',6'); 3.61, 1H (CH₃); ¹³C NMR (DMSO-*d*₆), δ 32.14, 1C (CH₃).

3-Ethyl-1,3-diphenyltriazene. Yield 67%. ¹H NMR (DMSO-*d*₆), δ 7.18, 1H (H-4'); 7.30, 1H (H-4); 7.44–7.49, 4H (H-3,5 and H-3',5'); 7.55–7.62, 4H (H-2,6 and H-2',6'); 1.23, 3H (CH₃); 4.34, 2H (CH₂); ¹³C NMR (DMSO-*d*₆), δ 10.94, 1C (CH₃); 40.29, 1C (CH₂).

3-Propyl-1,3-diphenyltriazene. Yield 65%. ¹H NMR (DMSO-*d*₆), δ 7.17, 1H (H-4'); 7.30, 1H (H-4); 7.43–7.49, 4H (H-3,5 and H-3',5'); 7.55–7.61, 4H (H-2,6 and H-2',6'); 0.94, 3H (CH₃); 1.68, 2H (CH₂); 4.25, 2H (CH₂); ¹³C NMR (DMSO-*d*₆), δ 11.28, 1C (CH₃); 18.87, 1C (CH₂); 45.38, 1C (CH₂).

3-Butyl-1,3-diphenyltriazene. Yield 54%. ¹H NMR (DMSO-*d*₆), δ 7.17, 1H (H-4'); 7.29, 1H (H-4); 7.40–7.48, 4H (H-3,5 and H-3',5'); 7.55–7.59, 4H (H-2,6 and H-2',6'); 0.94, 3H (CH₃); 1.38, 2H (CH₂); 1.65, 2H (CH₂); 4.32, 2H (CH₂); ¹³C NMR (DMSO-*d*₆), δ 13.72, 1C (CH₃); 19.83, 1C (CH₂); 27.63, 1C (CH₂); 43.56, 1C (CH₂).

3-Pentyl-1,3-diphenyltriazene. Yield 60%. ¹H NMR spectrum (DMSO-*d*₆), 7.16, 1H (H-4'); 7.28, 1H (H-4); 7.41–7.46, 4H (H-3,5 and H-3',5'); 7.53–7.57, 4H (H-2,6 and H-2',6'); 0.87, 3H (CH₃); 1.32, 2H (CH₂); 1.34, 2H (CH₂); 1.61, 2H (CH₂); 4.27, 2H (CH₂); ¹³C NMR (DMSO-*d*₆), δ 13.98, 1C (CH₃); 22.10, 1C (CH₂); 25.04, 1C (CH₂); 28.65, 1C (CH₂); 43.78, 1C (CH₂).

3-Isopropyl-1,3-diphenyltriazene. Yield 62%. ¹H NMR (DMSO-*d*₆), δ 7.24, 1H (H-4'); 7.35, 1H (H-4); 7.39–

7.52, 8H (H-3,5; H-3',5'; H-2,6 and H-2',6'); 1.38, 6H (CH₃); 5.63, 1H (CH); ¹³C NMR (DMSO-*d*₆), δ 20.11, 2C (CH₃); 49.89, 1C (CH).

3-sec-Butyl-1,3-diphenyltriazene. Yield 52%. ¹H NMR (DMSO-*d*₆), δ 7.15, 2H (H-4 and H-4'); 7.25–7.61, 8H (H-3,5; H-3',5'; H-2,6 and H-2',6'); 0.96, 3H (CH₃); 1.18, 3H (CH₃); 1.35–1.65, 2H (CH₂); 5.30, 1H (CH); ¹³C NMR (DMSO-*d*₆), δ 10.69, 1C (CH₃); 20.10, 1C (CH₃); 29.18, 1C (CH₂); 49.02, 1C (CH).

3-Cyclohexyl-1,3-diphenyltriazene. Yield 33%. ¹H NMR (DMSO-*d*₆), δ 7.08, 2H (H-4 and H-4'); 7.35–7.50, 8H (H-3,5; H-3',5'; H-2,6 and H-2',6'); 1.12–1.97, 10H (CH₂); 5.37, 1H (CH); ¹³C NMR (DMSO-*d*₆), δ 27.4, 1C (CH₂); 24.44, 2C (CH₂); 32.72, 2C (CH₂); 50.55, 1C (CH).

The starting *N*-alkylanilines were synthesized by the reduction of acylanilides with bis(2-methoxyethoxy)-aluminium hydride in toluene (ethyl and propyl), by alkylation of aniline according to Hickinbottom and co-workers^{25,26} with subsequent separation of the mixture (butyl, isopropyl, *sec*-butyl), by reductive amination of 1-pentan-ol with aniline²⁷ in the presence of Raney nickel catalyst (pentyl) and by the reduction of alkylideneaniline with lithium tetrahydridoaluminate (cyclohexyl). The *N*-methyl derivative was a commercial product.

Kinetic measurements. The kinetic measurements were based on spectrophotometric monitoring of the decrease in the absorbance of the respective triazene at 359 nm in hexane 25.5 °C using a Durrum D-110 stopped-flow spectrophotometer. One reservoir of the apparatus contained a solution of trichloroacetic acid in hexane (0.02–0.50 mol dm⁻³) and the other reservoir (of the same capacity) contained a solution of triazene in hexane of concentration such as to obtain a resulting absorbance of the reaction mixture after the rapid mixing of solutions from both reservoirs in the range 0.5–1.0 units. The solutions of the components and the cell compartment were kept at 25.5 ± 0.2 °C. The concentration of trichloroacetic acid was determined by reverse titration of the reaction mixture after its extraction in a double volume of aqueous sodium hydroxide of suitable concentration. Altogether 61–92 measurements were carried out for each derivative in the given concentration range of trichloroacetic acid. The observed rate constants, *k*_{obs}, were calculated from the reaction half-time read on the apparatus display. A reaction order of unity was verified for 3-propyl-1,3-diphenyltriazene by the method of initial concentrations.

Evaluation of experimental data. The mathematical–statistical modelling of the dependence of the observed rate constant, *k*_{obs}, on the concentration of trichloroacetic acid, *c*, was carried out by non-linear

regression using efficient optimization methods (genetic algorithm, simplex method, Levenberg–Marquardt method). The results were evaluated statistically, the statistically insignificant rate constants were omitted from the models and the calculation was repeated. The criteria for the selection of the most suitable model were the residual standard deviation and positive values of rate and equilibrium constants as the optimized parameters.

RESULTS AND DISCUSSION

Figures 1 and 2 present typical dependences of the observed rate constant, k_{obs} , of reaction of 3-alkyl-1,3-diphenyltriazenes on the concentration of trichloroacetic acid in hexane for the methyl and *sec*-butyl derivatives, respectively. The dependences of the observed rate

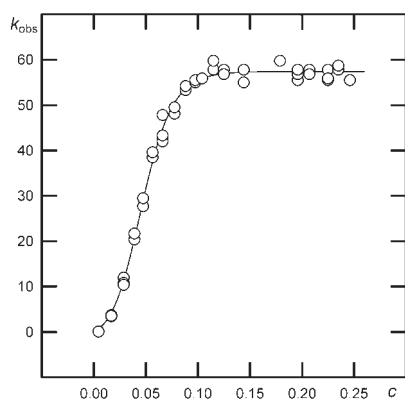


Figure 1. Dependence of observed rate constant, k_{obs} (s^{-1}), on concentration of trichloroacetic acid, c (mol dm^{-3}), for 3-methyl-1,3-diphenyltriene

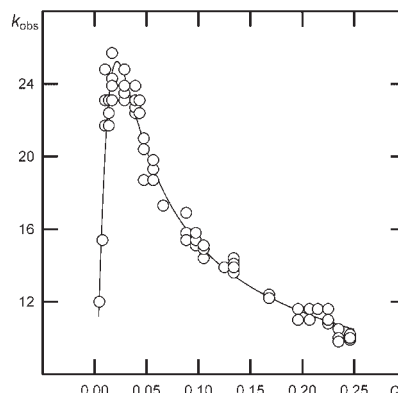
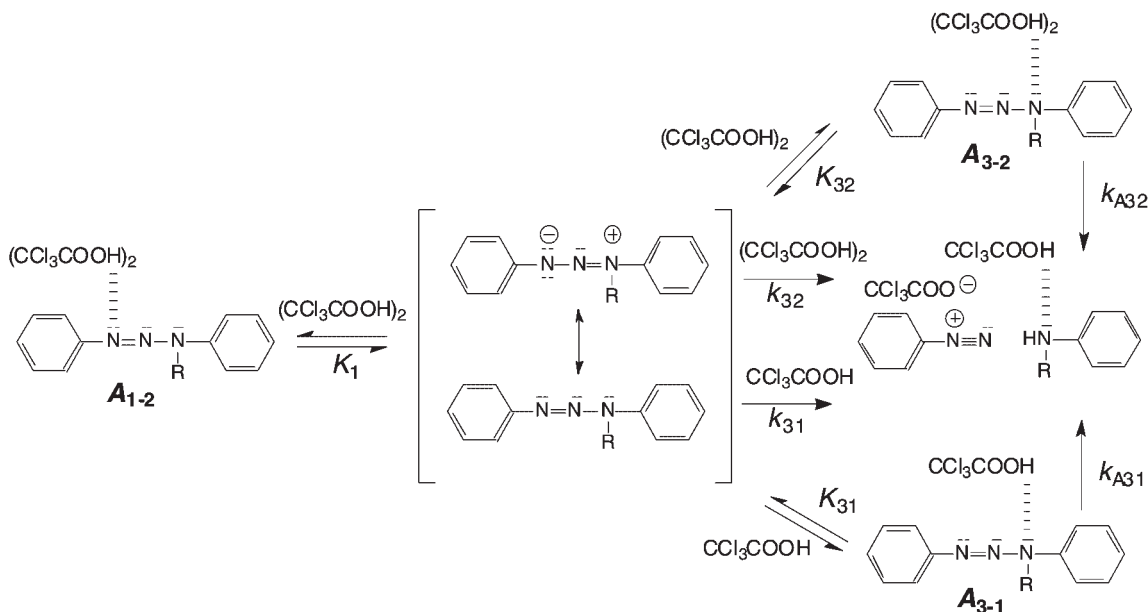


Figure 2. Dependence of observed rate constant, k_{obs} (s^{-1}), on concentration of trichloroacetic acid, c (mol dm^{-3}), for 3-*sec*-butyl-1,3-diphenyltriene

constant on concentration of trichloroacetic acid for ethyl, propyl, butyl and pentyl substituents are of identical type to those of the methyl derivative, whereas those of the isopropyl and cyclohexyl substituents are identical with those of the *sec*-butyl derivative. In the case of the cyclohexyl substituent, we failed to record experimentally the starting section of the curve. As can clearly be seen from the figures, the dependences have non-trivial courses.

Proposed kinetic model

Scheme 1 was the starting point for suggesting possible regression functions: it was derived from the known pieces of information concerning the reaction system, including the products (see Introduction). With regard to the non-polar medium, we assume the formation of less polar associates instead of polar ion pairs.



Scheme 1

The suggestion was based upon the presumption of identical reaction mechanisms for all the compounds studied, and the presumption of three basic factors affecting the experimental dependence of observed rate constant on trichloroacetic acid concentration, viz. the solvent, the substrate and the acid catalyst.

Hexane as a non-polar ($\epsilon_r = 1.91$) aprotic solvent²⁸ does not stabilize either polar transition states or polar products of an ionic nature. However, the properties of this medium can be changed by the addition of trichloroacetic acid (monomer, $\mu = 3.0$, Ref. 29) as a co-solvent. Experimental measurements in binary mixtures composed of a non-polar and a polar solvent showed³⁰ that the reacting system is preferably solvated by the more polar component, and the logarithm of the observed rate constant is a linear function of concentration over a broad concentration interval.³¹ Measurements³² of the acid-catalysed decomposition of 1,3-bis(4-methylphenyl)triazene by various organic acids in mixtures of hexane and the organic acid revealed an exponential increase in the observed rate constant at low concentrations of the organic acid used as the co-solvent. Therefore, it can be deduced for the system studied that the values of the logarithm of rate and equilibrium constants in Scheme 1 can depend on the trichloroacetic acid concentration in the reaction mixture,³³ especially at lower concentrations of the acid.

The properties the substrate in the series adopted are predominantly due to the distribution of electron density in nitrogen atoms of the triazene chain, and to inductive and steric effects of the alkyl groups. From quantum-chemical calculations,^{18–20} it can be presumed that the N1 and N3 atoms will be protonated (or, as the case may be, will form associates with the acid), which stands in accordance with the resonance formula given in Scheme 1. From configurational studies it is known that triazenes possess a *trans* configuration, and the *cis-trans* isomerization is subject to general acid and general base catalyses.¹⁷ The barrier to rotation around the N2—N3 bond of 1-phenyl-3,3-dialkyltriazenes in a non-polar solvent³⁴ depends little on the bulkiness of the alkyl substituent, and the molecule is almost planar. The mutual steric interaction between alkyl and phenyl groups in the 3-alkyl-1,3-diphenyltriazenes studied can, in principle, cause a deviation of the benzene ring from the common plane of the N1, N2, and N3 atoms. This can restrict or even prevent the delocalization of free electron pairs from the N3 atom into the benzene ring (steric hindrance to resonance), while the electron density of this atom can be contrastingly increased.

According to literature data,^{33,35} trichloroacetic acid predominantly exists as a dimer in non-polar solvents. The dissociation constant K_D of the dimer to monomer is low in non-polar solvents (e.g. $K_D = 0.0018$ in toluene; unknown for hexane). The dissociation of monomeric trichloroacetic acid to its conjugated base and proton is obviously negligible, and thus only the monomer, dimer

or higher associates of trichloroacetic acid can be taken in to account as the catalyst particles.

On the basis of the above considerations, we have created a systematic series of possible kinetic models and the respective regression functions for the interpretation of the measured dependences of the observed rate constant, k_{obs} , on the concentration of trichloroacetic acid, c . The models start from Scheme 1 and involve catalysis by monomeric and dimeric trichloroacetic acid, the potential formation of associates of trichloroacetic acid with the N1 and N3 atoms of triazene and a possible dependence of rate and equilibrium constants on the changes in properties of the reaction medium due to added trichloroacetic acid.

With the use of the criterion of the minimum residual standard deviation, the model in Eqn (1) was selected.

$$k_{\text{obs}} = \frac{K_1(k_{\text{HA}}[\text{HA}] + k_{\text{HA}2}[\text{HA}]^2)e^{gc}}{(1 + K_1[\text{HA}]^2e^{gc})} \quad (1)$$

where k_{HA} is the rate constant of reaction with participation of one molecule of trichloroacetic acid, $k_{\text{HA}2}$ is the rate constant of reaction with participation of two molecules of trichloroacetic acid, K_1 is the dissociation constant of associates of two molecules of trichloroacetic acid with N1 of triazene (A_{1-2} in Scheme 1) and g is the slope of the dependence describing changes in properties of the reacting system caused by the addition of trichloroacetic acid as a co-solvent. The introduction of an exponential term into the regression model was inevitable for a proper description of the onset part of the dependence at low concentrations of acid. The calculation with separate constants g for the individual rate and equilibrium constants in Eqn (1) proved that they are identical for a given substrate.

According to the literature,^{33,35} the dimer D is a dominating form of trichloroacetic acid in the given medium. Its concentration in solution can be expressed by

$$[\text{D}] = c/2 \quad (2)$$

The concentration of monomer, M, in the solution is given by Eqn (3)

$$[\text{M}] = \sqrt{K_D[\text{D}]} = \sqrt{K_D(c/2)} \quad (3)$$

where K_D is the dissociation constant of the dimer giving the monomer. After introducing the concentrations of monomer and dimer from Eqns (2) and (3) into Eqn (1), we obtain

$$k_{\text{obs}} = \frac{K_1[k_{\text{HA}}\sqrt{K_D}\sqrt{(c/2)} + k_{\text{HA}2}(c/2)]e^{gc}}{1 + K_1(c/2)e^{gc}} \quad (4)$$

The quality of fitting experimental points by the curves calculated from Eqn (4) is shown in Figs 1 and 2. The

Table 1. Number of measurements n of observed rate constants, values of rate constants $k_{\text{HA}}\sqrt{K_{\text{D}}}$ and $k_{\text{HA}2}$, values of dissociation constant K_1 and values of parameter g in Eqn (4), their standard deviations and residual standard deviation s (the constants not given are statistically insignificant)

Substituent	n	$k_{\text{HA}}\sqrt{K_{\text{D}}}$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	$k_{\text{HA}2}$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	K_1 ($\text{dm}^3 \text{mol}^{-1}$)	g ($\text{dm}^3 \text{mol}^{-1}$)	s (s^{-1})
CH_3	61		57.4 ± 0.3	4.22 ± 0.43	49.0 ± 2.1	1.39
CH_3CH_2	69		75.8 ± 0.5	4.67 ± 0.53	51.8 ± 2.7	2.70
$\text{CH}_3\text{CH}_2\text{CH}_2$	63		87.3 ± 0.3	4.97 ± 0.32	49.0 ± 1.5	1.68
$\text{CH}_3(\text{CH}_2)_2\text{CH}_2$	66		87.7 ± 0.5	5.44 ± 0.43	55.8 ± 2.1	2.23
$\text{CH}_3(\text{CH}_2)_3\text{CH}_2$	64		85.6 ± 0.4	6.37 ± 0.43	55.3 ± 1.8	1.89
$(\text{CH}_3)_2\text{CH}$	77	7.52 ± 0.12	5.92 ± 0.5	22.3 ± 2.9	140 ± 8	1.21
$\text{CH}_3\text{CH}_2(\text{CH}_3)\text{CH}$	79	2.86 ± 0.10	2.39 ± 0.4	72.8 ± 5.4	89.3 ± 8.5	0.983
cyclo C_6H_{11}	92	5.32 ± 0.04		219 ± 44	66.3 ± 13.3	1.14

values of statistically significant parameters in Eqn (4) and their standard deviations are presented in Table 1.

The course of observed rate constant, k_{obs} , on concentration of trichloroacetic acid, c , depends on the ratio of the magnitudes of the constants $k_{\text{HA}}\sqrt{K_{\text{D}}}$ (the reaction of triazene with the participation of one molecule of trichloroacetic acid), $k_{\text{HA}2}$ (the reaction of triazene with the participation of two molecules of trichloroacetic acid) and K_1 (the dissociation of non-reactive associate A_{1-2}). If K_1 is small, and $k_{\text{HA}2}$ is significantly greater than the product $k_{\text{HA}}\sqrt{K_{\text{D}}}$, then only the reaction with the participation of two molecules of trichloroacetic acid makes itself felt kinetically. The dependence for low concentrations of trichloroacetic acid increases approximately exponentially and forms a plateau at high concentrations (typically 1-methyl-1,3-diphenyltriazene, Fig. 1). This course was observed with all the 3-alkyl-1,3-diphenyltriazenes having linear alkyl groups (the constant $k_{\text{HA}}\sqrt{K_{\text{D}}}$ is statistically insignificant). For opposite ratios of the magnitudes of $k_{\text{HA}}\sqrt{K_{\text{D}}}$ and $k_{\text{HA}2}$, the kinetically dominant reaction is that involving one molecule of trichloroacetic acid. The dependence at low acid concentrations also increases almost exponentially, but at high concentrations there is a drop corresponding to the reciprocal of $\sqrt{c/2}$ (typically 3-sec-butyl-1,3-diphenyltriazene, Fig. 2). This course was observed with isopropyl and sec-butyl substituents. If K_1 is sufficiently high, and $k_{\text{HA}2}$ is negligible compared with the product $k_{\text{HA}}\sqrt{K_{\text{D}}}$, then the exponential increase is suppressed at low concentrations of trichloroacetic acid, and only the decrease corresponding to the reciprocal $\sqrt{c/2}$ is observed (as is the case with 3-cyclohexyl-1,3-diphenyltriazene; the constant $k_{\text{HA}2}$ is statistically insignificant).

Evaluation of effect of trichloroacetic acid as co-solvent

The necessity for involvement of the exponential term with parameter g in Eqn (4) indicates the effect of change in reaction medium on the reaction under study. A semi-empirical description of the dependence of the reaction

rate constant between neutral bipolar molecules of triazene and trichloroacetic acid on the properties of solvent can be expressed²⁸ by

$$\ln k = \ln k_0 - \frac{1}{4\pi\epsilon_0} \frac{N_{\text{A}}}{RT} \frac{\epsilon_{\text{r}} - 1}{2\epsilon_{\text{r}} + 1} \left(\frac{\mu_{\text{T}}^2}{r_{\text{T}}^3} + \frac{\mu_{\text{TAA,eff}}^2}{r_{\text{TAA,eff}}^3} - \frac{\mu_{\neq}^2}{r_{\neq}^3} \right) \quad (5)$$

where k is the rate constant k_{HA} or $k_{\text{HA}2}$ in the given medium, k_0 is the rate constant of the same reaction in the standard state, ϵ_{r} is the relative permittivity of the medium, μ_{T} is the dipole moment of triazene, $\mu_{\text{TAA,eff}}$ is the effective dipole moment of all forms of trichloroacetic acid in the given medium, $\mu_{\neq}$ is the dipole moment of the activated complex of reaction and r_{T} , $r_{\text{TAA,eff}}$ and $r_{\neq}$ are the radii of the corresponding particles. Formally identical is the description of the dependence of the equilibrium constant on the properties of solvent by

$$\ln K = \ln K_0 - \frac{1}{4\pi\epsilon_0} \frac{N_{\text{A}}}{RT} \frac{\epsilon_{\text{r}} - 1}{2\epsilon_{\text{r}} + 1} \left(\frac{\mu_{\text{T}}^2}{r_{\text{T}}^3} + \frac{\mu_{\text{TAA,eff}}^2}{r_{\text{TAA,eff}}^3} - \frac{\mu_{\text{A}}^2}{r_{\text{A}}^3} \right) \quad (6)$$

where K is the equilibrium constant (K_1 , K_{31} or K_{32} in Scheme 1) in the given medium, K_0 is the equilibrium constant in the standard state, μ_{A} is the dipole moment of the associate of triazene and trichloroacetic acid, r_{A} is its radius, and the other symbols are as in Eqn (5). The dependence of the Kirkwood function on the concentration of the polar co-solvent in the non-polar aprotic solvent is approximately linear;³⁶ for associating carboxylic acids it is sometimes necessary to add a quadratic term.^{37,38} In the narrow range of concentrations of trichloroacetic acid used, this dependence can be considered linear, i.e.

$$\frac{\epsilon_{\text{r}} - 1}{2\epsilon_{\text{r}} + 1} \approx \alpha c \quad (7)$$

where α is a constant of proportionality. The comparison of Eqns (4) and (5) or Eqns (4) and (6) taking into account Eqn (7) shows that parameter g in the exponential term of Eqn (4) is a measure of the difference between polarities of the transition state and the educts, or that between the polarities of the associate and its components.

As already stated, the found values of parameter g are positive for a given substitution derivative (Table 1) and identical in both the numerator and denominator of kinetic model (4), hence they are obviously due to the same process. From the form of the kinetic model (4), it follows that the exponential term is connected with the dissociation constant K_1 , whereas the rate constants k_{HA} and k_{HA2} are independent of the parameter g . The dependence of the dissociation constant K_1 on changes in the properties of the solvent is, according to Eqn (6), given by the difference between the polarities of the components in this equilibrium. As the dipole moment of trichloroacetic acid dimer (predominating form in the reaction mixture) is approximately zero³⁸ and that of triazene³⁹ is low ($\mu = 0.79$), obviously in the respective associate the proton is transferred to a considerable extent. On the other hand, the absence of the effect of the change of the medium on the rate constants k_{HA} and k_{HA2} according to Eqn (5) indicates a small difference in polarities of the educts and the activated complex. Therefore, it can be deduced that the reacting species is probably the polar monomer of trichloroacetic acid ($\mu = 3.0$)²⁹ or the open dimer, the proton being transferred to the substrate to only a small extent in the transition state.

Evaluation of substitution effects

The dependence of the logarithm of the dissociation constant K_1 on substitution is quantitatively described by

$$\log K_1 = -(0.435 \pm 0.160) + (1.83 \pm 0.25)\nu + (0.444 \pm 0.117)Ind \quad (8)$$

$$n = 8, R = 0.993, s = 9.28 \times 10^{-2}, F(2, 5) = 169.6$$

where ν are the Charton constants for the description of the steric effects of substituents,⁴⁰ Ind is the indicator variable taking into account the differences between straight- and branched-chain alkyls (Ind being 0 and 1 for the former and latter, respectively), n is number of points, s is residual standard deviation and F is the criterion of statistical significance of the explaining variables in the regression. From Eqn (8), it is obvious that the dissociation constant K_1 depends exclusively on steric effects, whereas the inductive effect described by the constant σ^{i41} is statistically insignificant. Therefore, it follows that trichloroacetic acid molecules are associated at such a site of triazene that is separated by several bonds from the substitution site. This confirms the original

presumption that the associate is A_{1-2} in Scheme 1. The constant characterizing sensitivity to steric effects is positive, and the branching of alkyl (described by the indicator variable Ind) increases the value of the dissociation constant K_1 even more. From what has been said, it follows that a dominating part in the formation of associate A_{1-2} is played by steric effects, which lower the stability as expected.

The dependence of the logarithm of rate constant k_{HA2} from Table 1 is quantitatively described by Eqn (9) for all the substituents except cyclohexyl (where k_{HA2} is statistically insignificant):

$$\log k_{HA2} = (1.74 \pm 0.24) - (25.6 \pm 7.3)\sigma^i - (1.90 \pm 0.51)\nu - (1.14 \pm 0.11)Ind \quad (9)$$

$$n = 7, R = 0.998, s = 1.68 \times 10^{-2}, F(2, 4) = 586.3$$

where σ^i are substituent constants⁴¹ describing the inductive effect and the other symbols are as in Eqn (8).

The reaction constant describing the inductive effect is negative and very large. Its sign is in accordance with the mechanism involving the splitting off of electrofuge (diazonium cation) in the rate-limiting step of the reaction. The magnitude of the reaction constant indicates a high sensitivity to changes in electron density at the reaction centre. The reaction constant describing steric effects is again negative, as expected, and its magnitude is comparable to that in Eqn (8). However, as the attack by reagent takes place at the atom carrying the substituent, the steric effects should make themselves felt more markedly. Therefore, it can be deduced that the reaction does not go via associates A_{3-1} and A_{3-2} (Scheme 1) but proceeds in a single reaction step. The arrangement of the activated complex is less organized in comparison with associate A_{1-2} , and the proton transfer to substrate is less advanced. This conclusion is in accordance with the above-mentioned conclusion following from the interpretation of the change of medium on the rate constants k_{HA} and k_{HA2} .

The values of rate constant $k_{HA}\sqrt{K_D}$ of the reaction with the monomer are statistically significant only for branched-chain alkyls. The values of $k_{HA}\sqrt{K_D}$ decrease with increasing substituent constant σ^i , in the same way as with the constant k_{HA2} [Eqn (9)]. Therefore, it can be deduced that the reaction course is similar, but this hypothesis is impossible to verify quantitatively owing to the small number of substituents studied.

The dependence of the values of the parameter g (describing the effect of change of medium on the dissociation constant K_1) on the Charton constants⁴⁰ ν is represented in Fig. 3. The picture clearly shows the difference between linear and branched alkyls as substituents. The values of g for branched-chain alkyls are higher and (in contrast to those of linear-chain alkyls) depend markedly on the bulkiness of the substituent. This can be caused by the above-mentioned (see Introduction)

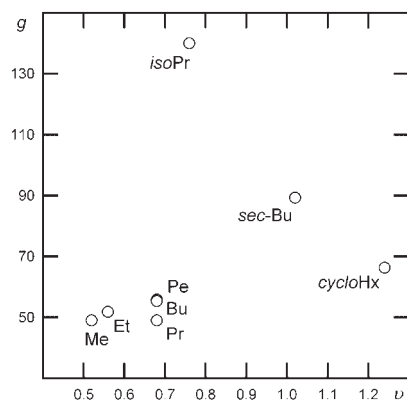


Figure 3. Dependence of parameter g (dm³ mol⁻¹) in Eqn (4) on steric constants ν

sterically forced deviation of the phenyl group out of the plane of the triazene chain due to the branched alkyl substituents. Owing to steric hindrance to resonance of the free electron pair at the N3 atom with the benzene nucleus, the electron density at this atom is increased, and owing to resonance, the electron density at N1 is also increased and, as a consequence, also the polarity of associate A₁₋₂.

CONCLUSIONS

The course of the dependence of observed rate constant k_{obs} on the concentration c of trichloroacetic acid for triazenes substituted with branched-chain alkyl groups shows that the amount of the reactive form of triazene decreases with increasing acid concentration. This finding was explained by the formation of a non-reactive associate of trichloroacetic acid with triazene at the N1 atom taking place in a side equilibrium. The kinetic model (4) found involves the reaction of triazene with one and two molecules of trichloroacetic acid. The interpretation of the solvent and inductive effects shows that the triazene reacts with monomer and obviously with the open dimer of trichloroacetic acid in a single reaction step, the proton transfer to substrate being little advanced in the activated complex. In this interpretation, the rate constants k_{HA} and $k_{\text{HA}2}$ in kinetic model (4) are identical with the rate constants k_{31} and k_{32} in Scheme 1.

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