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Thermodynamics of the Protonation and Ultra-violet Absorption of 1,2,4-Triazole in Aqueous Solutions and a Method for Testing the Reliability of a Weak n—π^* Transition Band from a Protonable Compound

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The first and second protonation constants of 1,2,4-triazole were determined potentiometrically in aqueous sodium perchlorate solutions at 15, 20, 25, and 35 °C. The thermodynamic protonation constants were obtained by extrapolation to zero ionic strength and the thermodynamic quantities, the free energies, enthalpies, entropies, and heat capacities of the protonation equilibria were calculated from these.

The ultra-violet and visible absorption of 1,2,4-triazole was studied in aqueous, ethanol and hexane solutions. The absorption band due to $\pi-\pi^*$ transition in the range 185–210 nm only was observed in the spectrum. Our studies show that calculations of the log K values from the absorption spectra in water solutions may be used to decide the existence or non-existence of the $n-\pi^*$ excitation band in the spectrum of a protonable compound. The results are discussed below.

1,2,4-Triazole belongs to the group of the five-membered heterocyclic ring compounds. The ring structure contains three nitrogen atoms and its crystal structure has been determined.[1] According to its structure, 1,2,4-triazole may exist in two tautomeric forms [1–3] depending on whether the hydrogen atom is bonded to nitrogen at the position 1 or 4. On the basis of the potentiometric titration curves and the ultraviolet spectra it may be conluded that within the potentiometrically measurable range 1,2,4-triazole shows two prevailing protonation equilibria. In an alkaline solution hydrogen bonded to the nitrogen atom is left as a proton; and in an acid solution, a proton is added to the nitrogen atom at position 2 or 4 (most probably position 4) in the case of 1H-1,2,4-triazole, and at position 1 or 2 (which are equivalent in this respect, the C_{2v} molecular symmetry) in the case of 4H-1,2,4-triazole. More detailed decision between the different equilibria of the tautomers is not possible on the basis of the potentiometric or UV-spectrophotometric studies of the unsubstituted 1,2,4-triazole as shown in the present study.

Furthermore the effect of a neutral salt on the protonation equilibria of 1,2,4-triazole was studied by performing measurements in aqueous sodium perchlorate solutions at different ionic strengths and temperatures (not done previously), because they were needed in our studies on complexation of 1,2,4-triazole with transition metal ions.

The recorded absorption spectra gave also a possibility to consider the reliability of the $n-\pi^*$ transition bands in heterocyclic compounds from a new viewpoint as described below.

EXPERIMENTAL

Reagents and solutions. A distilled, deionized and carbonate free water was used in the preparation of the solutions. Sodium perchlorate (G. Frederic Smith Chemical Co.) was purified as described previously.[4,5] Sodium and potassium hydroxides (Titrisol), boric acid potassium biphthalate, potassium chromate, conc. perchloric acid and sodium chloride were all guaranted reagents of E. Merck, AG. Heptane and hexane were also guaranteed

reagents of E. Merck, AG., and ethanol was of the quality AaS (Oy Alko Ab).

For preliminary experiments we used 1,2,4-triazole of L. Light & Co. The producer gives the quality as: pure, assay ≥ 96 % (titration ex basic nitrogen), m.p. 120–121 °C. In the potentiometric and spectrophotometric measurements reported in the present paper we used 1,2,4-triazole of EGA-Chemie KG. The producer gives in this case as quality data: M.p. 119.5–121 °C, IR: ok, 99 % (T). Weighed amounts of the compound were dissolved in excess sodium hydroxide solutions and titrated potentiometrically with a known mineral acid solution (HCl or $HClO_4$). From the acid consumption difference between the two turning points of the titration curve the purity of the compound was found to be 100.4 ± 0.5 %. The compound was used as 100 %. The error due to this in the potentiometric determinations of the protonation constants falls within experimental errors. Its effect on the spectrophotometric measurements in the range 185–240 nm at low concentrations is given under experimental errors and the effect in the range 230–300 nm is discussed later.

Infra-red spectra of both samples of 1,2,4-triazole were run in KBr disks (1 mg of 1,2,4-triazole/400 mg of KBr (Uvasol, E. Merck, AG.)) on a Perkin-Elmer Model 457 spectrophotometer in the wavelength range 4000–250 cm^{-1}. The spectra were compared with the spectrum (No. 29293 K) of 1,2,4-triazole (Aldrich Chemical Co.) reported in the collection of the Sadtler Standard Infra-red Grating Spectra. Both spectra showed a medium broad band at 3420 cm^{-1} obviously due to the OH stretching vibrations of water, perhaps absorbed from the atmosphere. Weak bands were observed further at 1630 and 630 cm^{-1} and the weak band at 722 cm^{-1} was missing. The EGA-Chemie product showed more very weak bands at 1347 and 1237 cm^{-1}. Most probably the observed extra bands are due to C=O (COO) stretching vibrations (*cf.* Ref. 26, pp. 53, 69, 108, and 110) and point to the presence of some carbonyl (carboxyl) containing impurity in minor amounts in both samples of 1,2,4-triazole used. This is the compound X referred to later in this paper.

About 0.1 M sodium hydroxide solutions were prepared in an atmosphere of nitrogen in airtight burette systems of Pyrex glass. The alkalinities of the solutions were determined against potassium biphthalate by potentiometric titrations.

A perchloric acid solution of about 0.3 M was diluted from conc. acid. The acidity of the solution was determined by potentiometric titrations with the before mentioned alkali solution.

The concentrations of the sodium perchlorate solutions were determined by means of the evaporation and ion exchange methods described previously.[5]

Solutions 0.005 M in $HClO_4$, 0.01 M in NaCl and $(I - 0.015)$ M in $NaClO_4$ were used as reference buffers. The titrant was 0.1 M in $HClO_4$, 0.01 M in NaCl and $(I - 0.11)$ M in $NaClO_4$.

The measuring flasks, burettes and pipettes were checked at 20 °C. Corrections of the concentrations due to the temperature expansion of the solutions were estimated by assuming the temperature expansion of the solutions to be that of pure water.[6]

Apparatus and measurements. The potentiometric titrations were performed in an atmosphere of nitrogen in gastight Pyrex vessels and in a water thermostat at 15, 20, 25, and 35 ± 0.01 °C. A glass electrode (Beckman, No. 41260) and a calomel electrode of the immersion type were used in connection with a potentiometer (Radiometer PHM 4). To 100 ml (20 °C) of the studied solution, 3.5–6.5 or 13.5–16.5 ml of the titrant solution were added with 0.5 ml increments, and after magnetic stirring of the solution the potentials were read to ± 0.2 mV. The titrations were performed as duplicates and therefore each value of log K is a mean value from about 14 measurements. The potentials were stabilized within a few minutes. The electrode system was checked against the reference buffer in the beginning and end of each titration. The measuring cells may be presented schematically as follows (20 °C):

Glass electrode	100 ml 0.01 M 1,2,4-Triazole 0.01 M NaCl 0.01 M NaOH $(I - 0.02)$ M $NaClO_4$	
	0.01 M NaCl $(I - 0.01)$ M $NaClO_4$	Hg_2Cl_2, Hg

The ultraviolet spectra of 1,2,4-triazole in the different solutions were recorded with a Hitachi Perkin-Elmer Model 124 Doublebeam Grating Spectrophotometer at room temperature (about 22 °C). Control measurements were performed with a Beckman Model DU-2 Ultraviolet Spectrophotometer at 25 ± 0.1 °C. A flowing nitrogen atmosphere was used within the equipment. The spectrophotometers were calibrated with an alkaline potassium chromate solution (0.04 g of potassium chromate in 1 l of 0.05 M potassium hydroxide).[7] Quartz cuvettes of 1 cm optical lengths were used and compared, each one being substituted for the other in turn. The absorbance differences between the cuvettes were less than 0.01 unit. The background of the Coleman spectrophotometer increased from zero (at 370 nm) to 0.02 unit (at 200 nm) with the slit position of 1 mm. The measured absorbances were

corrected for these error sources. The reference solutions were in other respects similar to the studied solutions, but contained no 1,2,4-triazole. The aqueous solutions were made after spectrophotometric measurements 0.02 M in sodium chloride (at 20 °C) before the pH ($= -\log_{10}[H^+]$) values of the solutions were measured as described above.

RESULTS AND DISCUSSION

Potentiometric part. When the minor equilibria due to the different tautomers are neglected, the prevailing protonation equilibria in aqueous solutions of 1,2,4-triazole may be presented as follows:

$$L^- + H_3O^+ \rightleftharpoons HL + H_2O \quad (1)$$

$$HL + H_3O^+ \rightleftharpoons H_2L^+ + H_2O \quad (2)$$

The corresponding protonation constants are

$$K_1 = [HL]/[L^-]\,[H^+] \quad (3)$$

$$K_2 = [H_2L^+]/[HL]\,[H^+] \quad (4)$$

Observing that the values of K_1 and K_2 differ so much from each other that they can be determined separately, and taking into account the total concentrations and the electroneutrality principle, it is easily derived for the logarithms of the constants

$$\log K_1 = \mathrm{pH} - \log\,[(C_B - C_{HClO_4} - [OH^-])/(C_{HL} + [OH^-] + C_{HClO_4} - C_B)] \quad (5)$$

$$\log K_2 = \mathrm{pH} + \log\,[(C_{HClO_4} - [H^+] - C_B)/(C_{HL} + [H^+] + C_B - C_{HClO_4})] \quad (6)$$

where C_{HL}, C_B, and C_{HClO_4} are the total concentrations of 1,2,4-triazole, the added sodium hydroxide, and perchloric acid, respectively. The hydrogen and hydroxide ion concentrations were each in turn neglected depending on the experimental conditions used to determine the protonation constants.

Table 1. The values of log K_1 and log K_2 of 1,2,4-triazole at different ionic strengths and temperatures. The values of pK_W, log K_1' and Δ log K_1 are given also.

°C	I	pK_W	Mean log K_1'	Mean Δ log K_1	Mean log K_1	Mean log K_2
15	0.120	14.132	10.048	0.008	10.056	2.422
20	0.120	13.952	9.929	0.008	9.937	2.397
25	0.119	13.779	9.810	0.009	9.819	2.340
35	0.119	13.458	9.576	0.012	9.588	2.272
15	0.250	14.096	10.031	0.006	10.037	2.527
20	0.250	13.915	9.904	0.008	9.912	2.477
25	0.249	13.742	9.794	0.010	9.804	2.450
35	0.249	13.421	9.578	0.012	9.590	2.395
15	0.500	14.084	10.080	0.008	10.088	2.599
20	0.500	13.903	9.960	0.009	9.969	2.581
25	0.499	13.729	9.832	0.010	9.842	2.534
35	0.497	13.408	9.591	0.013	9.604	2.455
15	0.750	14.097	10.132	0.011	10.143	2.694
20	0.750	13.915	10.014	0.013	10.027	2.661
25	0.748	13.742	9.897	0.014	9.911	2.599
35	0.746	13.420	9.629	0.016	9.645	2.512
15	1.000	14.120	–	–	10.191	2.754
20	1.000	13.938	–	–	10.062	2.718
25	0.998	13.764	–	–	9.938	2.671
35	0.995	13.441	–	–	9.693	2.594
15	2.001	14.246	10.456	0.007	10.463	3.068
20	2.000	14.061	10.330	0.009	10.339	3.022
25	1.996	13.885	10.195	0.010	10.205	2.952
35	1.991	13.557	9.918	0.012	9.930	2.844

The values of K_1 and K_2 were calculated from eqns. (5) and (6) in aqueous sodium perchlorate solutions at different temperatures on the basis of the potentiometric titration data. The mean values of log K_1 and log K_2 calculated are given in Table 1. In the calculation of K_1 the ionic product of water, K_w is needed. The values for this are not known, however, in aqueous sodium perchlorate solutions at different ionic strengths and temperatures. Therefore the values of log K_1' in Table 1 were calculated on the basis of the thermodynamic values of $pK_w°$: 14.346 (15 °C), 14.167 (20 °C), 13.996 (25 °C) and 13.680 (35 °C).[8] To take the salt effect into account at least to some extent, the dependence of K_w on the ionic strength in aqueous sodium perchlorate solutions at different temperatures was assumed to be the same as in aqueous potassium chloride solutions The values of pK_w calculated on this basis from an equation presented by Harned and Owen [9] are also given in Table 1. On the basis of these values in the lowest and highest titrations points, calculated correction terms for K_1 are given as mean values Δ log K_1 in Table 1. In the ionic strength 1.00 the values of K_1 were calculated using the values of K_w at each titration point.

The values of log K_1 and log K_2 may be represented as functions of the ionic strength by the equations:

$$\log K_1 = \log K_1° - 2A\sqrt{I}/(1+\alpha_1\sqrt{I}) + B_1 I \quad (7)$$

$$\log K_2 = \log K_2° + B_2 I \quad (8)$$

where for constant A the values 0.5028 (15 °C), 0.5070 (20 °C), 0.5115 (25 °C) and 0.5211 (35 °C) were used (Ref. 8, p. 406). The data for log K_1 and log K_2 (Table 1) were fitted by the method of least squares to eqns. (7) and (8). In the case of log K_2 the values at the lowest ionic strength ($I = 0.12$) were disregarded in these calculations, because of their obvious incorrectness due to the diffusion potentials. The results of the calculations are given in Tables 2 and 3. The values of log K_1 and log K_2 are represented as functions of the ionic strength at different temperatures in Figs. 1 and 2.

Table 2. The values of the constants α_1, B_1, and log $K_1°$ of eqn. (7) and B_2 and log $K_2°$ of eqn. (8) at different temperatures.

°C	α_1	B_1	log $K_1°$	B_2	log $K_2°$
15	2.191	0.2980	10.205	0.3087	2.450
20	2.190	0.2968	10.083	0.3038	2.418
25	2.250	0·2852	9.972	0.2845	2.386
35	2.003	0.2706	9.768	0.2599	2.327

Table 3. The values of the logarithms of the first (K_1) and second (K_2) protonation constants of 1,2,4-triazole calculated from eqns. (7) and (8) using the constants given in Table 2.

°C	I	$\sqrt{I}$	log K_1 eqn. (7)	log K_2 eqn. (8)
15	0.120	0.346	10.043	2.487
	0.250	0.500	10.039	2.528
	0.500	0.707	10.075	2.605
	0.750	0.866	10.128	2.682
	1.000	1.000	10.188	2.759
	2.001	1.414	10.454	3.068
20	0.120	0.346	9.919	2.454
	0.250	0.500	9.915	2.494
	0.500	0.707	9.950	2.570
	0.750	0.866	10.002	2.646
	1.000	1.000	10.062	2.722
	2.000	1.414	10.327	3.026
25	0.119	0.346	9.807	2.420
	0.249	0.499	9.802	2.457
	0.499	0.706	9.836	2.528
	0.748	0.865	9.885	2.599
	0.998	0.999	9.942	2.670
	1.996	1.413	10.195	2.954
35	0.119	0.345	9.587	2.358
	0.249	0.499	9.575	2.392
	0.497	0.705	9.598	2.457
	0.746	0.864	9.640	2.521
	0.995	0.997	9.690	2.586
	1.991	1.411	9.922	2.845

For comparison we have collected in Table 4 the protonation constant values of 1,2,4-triazole and of related five-membered nitrogen containing heterocycles, pyrrole, pyrazole, imidazole, 1,2,3-triazole, and tetrazole found in the literature. By comparing the values of the protonation constants of 1,2,4-triazole (Table 4) determined by different authors and mainly by the potentiometric method, they are found to be of the same order of magnitude.

When considering the reliability of the protonation constant values obtained in the present study we can say that while the potentials were read to ± 0.2 mV this corresponds to an accuracy of about ± 0.01 unit in the log K_n values. Generally the stabilization of the cell system was good, and only such

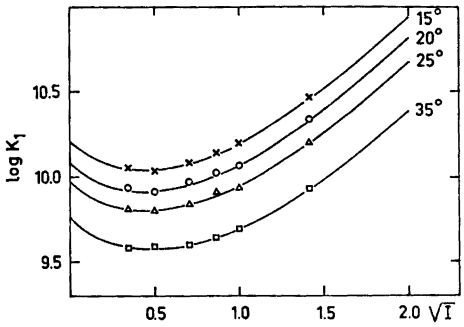

Fig. 1. The log K_1 values of 1,2,4-triazole as functions of the ionic strength in aqueous sodium perchlorate solutions at 15, 20, 25, and 35 °C.

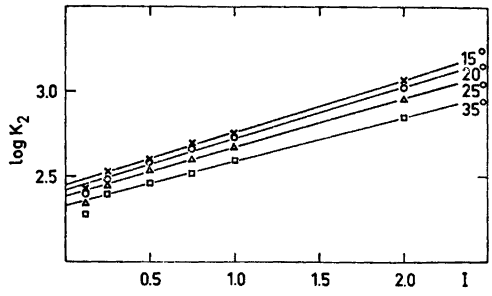

Fig. 2. The log K_2 values of 1,2,4-triazole as functions of the ionic strength in aqueous sodium perchlorate solutions at 15, 20, 25, and 35 °C.

titration results were used in the calculations. Using the ionic product values of pure water a drift of about 0.02 unit was observed in the calculated values of log K_1, whereas it was about 0.01 unit when the corrected values of the ionic product were used (Table 1). In the values of log K_2 the titration error was about ± 0.005 unit. To obtain a higher reliability the titrations were performed as duplicates.

Kröger and Freiberg [16] have compared the protonation constants of 1,2,4-triazole and its derivatives at 20 °C using Hammett's method and Hansen *et al.*[14] observed a linear dependence between the log K_1 values and the number of the nitrogen atoms in the five-membered heterocycles. The values of log K_2 in Table 4 do not show this behaviour, and

Table 4. Comparison of the values of the protonation constants of some unsaturated, five-membered nitrogen heterocycles in water.

Compound	°C	Ionic strength (added salt)	Method	log K_1	log K_2	Ref.
Pyrrole	20–25	?	spectrophotom.	–	−0.27	10
		?		16.5	–	11a
		12.4 ± 0.2 (KOH)		17.51 ± 0.05	–	11b
Pyrazole	25	0.025		–	2.47	12a
	25	?		14	–	13
	25	→0	glass el.	–	2.61	14
	20–25	1.2 ± 0.2 (KOH)	spectrophotom.	14.21	–	11b
	25.5 ± 0.5	→0	glass el.	–	2.52	12b
Imidazole	25	→0	glass el.	–	6.95	5
	25	→0	spectrophotom.	14.2	–	13, 15
	20–25	1.11 ± 0.05 (KOH)		14.17	–	11b
1,2,3-Triazole	20	→0	potentiometric	9.42	1.17	13
	25	→0	glass el.	9.26 ± 0.02	–	17
1,2,4-Triazole	20–25	?	spectrophotom.	–	2.30	12a
	20	0.005	glass el.	10.26	2.27	16,3
	25	→0		10.04	2.45	14
	20	→0		10.08	2.42	This work
	25	→0		9.97	2.39	
Tetrazole	room	~0.0033	potentiometric	4.89	–	18
	25	→0	glass el.	4.90	–	14
	25	?	potentiometric	4.79	–	19

therefore there exists no general (linear) dependence of the protonation tendency on the number of the nitrogen atoms in the five-membered heterocycles. Neither is any general dependence found between the values of log K_1 and log K_2. On the other hand all abovementioned heterocycles may form a one-charge anion that is protonated according to eqn. (1). With pyrrole the anion formation occurs only with difficulty and in very highly alkaline solutions as seen in Table 4. Pyrazole and imidazole are in this respect almost alike, but also form anions only in strongly alkaline solutions, whereas among the other compounds this tendency increases in the order 1,2,4-triazole, 1,2,3-triazole, and tetrazole (Table 4). So, the protonation tendency of the anions decreases generally in the order: pyrrole > pyrazole > imidazole > 1,2,4-triazole > 1,2,3-triazole > tetrazole. On the other hand the protonation tendency of the neutral molecules increases in the order: tetrazole < pyrrole < 1,2,3-triazole < 1,2,4-triazole < pyrazole < imidazole.

As pointed out above 1,2,4-triazole may exist in two tautomeric forms, and Kröger and Freiberg [3] have shown the tautomeric ratio of (1*H*)- to (4*H*)-1,2,4-triazole to be about 5 – 10:1. Therefore the almost identical protonation tendency of the neutral forms of pyrazole and 1,2,4-triazole (Table 4) is to be understood, whereas the inclusion of the third nitrogen atom in 1,2,3-triazole causes a decrease of the protonation tendency (a lower log K_2 value). The protonation tendency is further weakened by bringing the fourth nitrogen atom into the ring in tetrazole, for which a K_2 value has not so far been determined.

No unambiguous relation was found between the values of log K_1 or log K_2 given in Table 4 and the electron densities $\varrho\pi$ or $\varrho(\sigma+\pi)$ of the expected proton adding nitrogen atoms.[20,21] But the general tendency is, however, that the higher the electron density of the proton-adding nitrogen atom in the ring, the higher the value of log K_n.

The thermodynamic values of the protonation constants of 1,2,4-triazole were assumed to depend on the absolute temperature according to the equation:[22]

$$\log K_n^\circ = -(a/T) - cT + b \qquad (9)$$

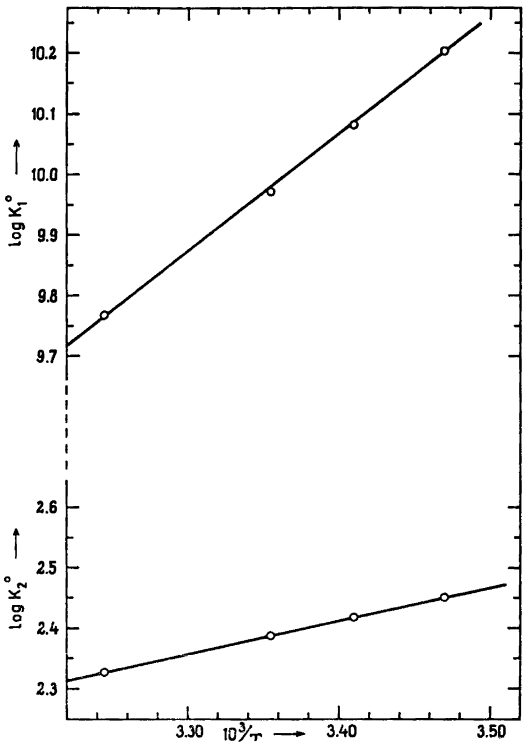

Fig. 3. The log K_1° and log K_2° values of the protonation constants of 1,2,4-triazole as functions of $1/T$.

(although a linear dependence on the temperature could be assumed as well (*cf.* Fig. 3)). The values of the constants a, b, and c given in Table 5 were calculated by fitting the experimental values of the constants log K_n° in Table 2 by the method of least squares to the equation. The log K_n° values of the thermodynamic protonation constants of 1,2,4-triazole are represented as functions of the reciprocal values of the absolute temperature in Fig. 3.

Table 5. The values of the constants a, b, and c of eqn. (9) for log K_1° and log K_2° of 1,2,4-triazole.

log K_n°	$-a \times 10^{-3}$	$-b$	$-c \times 10^3$
log K_1°	4.549	14.076	29.481
log K_2°	0.7613	0.881	2.393

Table 6. The values of log $K_1°$ and log $K_2°$ calculated from eqns. (7)–(9) and the corresponding free energies, enthalpies, and entropies of the protonation equilibria of 1,2,4-triazole at the temperatures used. The values of $T\Delta S°$ and $|10^2 T\Delta S°/\Delta G°|$ are given also.

°C	log $K_1°$ (eqn. (7))	log $K_1°$ (eqn. (9))	$-\Delta G°$ (kJ mol^{-1})	$-\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J K^{-1} mol^{-1})	$T\Delta S°$ (kJ mol^{-1})	$\lvert\frac{10^2 T\Delta S°}{\Delta G°}\rvert$
15	10.205	10.206	56.31	40.2	55.8	16.1	29
20	10.083	10.084	56.60	38.6	61.5	18.0	32
25	9.972	9.971	56.93	36.9	67.1	20.0	35
35	9.768	9.771	57.65	33.5	78.4	24.2	42
Mean at 15–35 °C			56.87 ± 0.4	37.3 ± 2	65.7 ± 7		

°C	log $K_2°$ (eqn. (8))	log $K_2°$ (eqn. (9))	$-\Delta G°$ (kJ mol^{-1})	$-\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J K^{-1} mol^{-1})	$T\Delta S°$ (kJ mol^{-1})	$\lvert\frac{10^2 T\Delta S°}{\Delta G°}\rvert$
15	2.451	2.451	13.52	10.8	9.5	2.75	20
20	2.418	2.417	13.57	10.6	10.0	2.93	22
25	2.386	2.386	13.62	10.5	10.5	3.12	23
35	2.327	2.327	13.73	10.2	11.4	3.50	26
Mean at 15–35 °C			13.61 ± 0.07	10.5 ± 0.2	10.3 ± 0.6		

The thermodynamic quantities, the free energies, enthalpies, entropies, and heat capacities of the first and second protonation equilibria of 1,2,4-triazole were then calculated from the equations:

$$\Delta G° = 2.303\, R(a - bT + cT^2) \quad (10)$$

$$\Delta H° = 2.303\, R(a - cT^2) \quad (11)$$

$$\Delta S° = 2.303\, R(b - 2cT) \quad (12)$$

$$\Delta C_p° = -4.606\, RcT \quad (13)$$

where $T = 273.16 + t$ °C and $R = 8.31433$ J K^{-1} mol^{-1}. The values of the thermodynamic quantities are given in Table 6, except for $\Delta C_p°$ for which only approximate mean values 330 and 27 J K^{-1} mol^{-1} were calculated for the first and second protonation reactions in the temperature range used.

From Table 6 it can be seen that $\Delta H°$ and $\Delta S°$ increase with increasing temperature for both protonation equilibria, which are exothermic processes. The temperature increase does not favour the protonation processes. The $|10^2 T\Delta S°/\Delta G°|$ values increase linearly with increasing temperature and more rapidly for the first protonation process, which means a higher increase of the effect of the entropy factor. The values show also that the enthalpy factor is dominant as compared with the entropy factor in the protonation processes, which are more dependent on the innermolecular (*e.g.* N–H bond energies) effects than on the environmental (solvation) changes.

The second (P.L.) of the present authors has previously compared the thermodynamic quantities associated with the ionization processes of some nitrogen-containing open-chain molecules.[23] The studied compounds were divided into two series, those in which a neutral molecule and those in which a negative monovalent ion were formed.[23] A similar interesting series of compounds form the nitrogen containing five-membered ring heterocycles mentioned above and under consideration here.

The thermodynamic data of the protonation equilibria of these compounds are, however, incomplete; those found in the literature were collected for comparison in Table 7. Also in this case when considering the $|10^2 T\Delta S°/\Delta G°|$ values against the $\Delta G°$ values, the protonation process of the negative monovalent ion forms shows higher $|10^2 T\Delta S°/\Delta G°|$ values than the protonation process of the neutral molecules, although the relations are not so smooth as with the open-chain nitrogen compounds,[23] but they point to the decrease of the entropy effect with increasing $\Delta G°$. On the contrary the enthalpy effect increases with increasing

Table 7. Comparison of the thermodynamic quantities, free energies, enthalpies, and entropies and the $|10^2 T\Delta S^\circ/\Delta G^\circ|$ values of the protonation equilibria of some unsaturated, five-membered nitrogen heterocycles in water at 25 °C.

Compound	log K_1°	$-\Delta G^\circ$ (kJ mol^{-1})	$-\Delta H^\circ$ (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})	$T\Delta S^\circ$ (kJ mol^{-1})	$\lvert\frac{10^2 T\Delta S^\circ}{\Delta G^\circ}\rvert$	Ref.
1,2,3-Triazole	9.26 ± 0.02	52.9 ± 0.1	37.2 ± 0.1	52.7	15.7	30	17
1,2,4-Triazole	9.97 ± 0.02	56.9 ± 0.2	36.9 ± 2	67.1	20.0	35	This work
	10.04 ± 0.05	57.3 ± 0.3	33.1 ± 0.9	81.2	24.2	42	14
Tetrazole	4.90 ± 0.01	28.0 ± 0.06	12.9 ± 0.3	50.6	15.1	54	14

Compound	log K_2°	$-\Delta G^\circ$ (kJ mol^{-1})	$-\Delta H^\circ$ (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})	$T\Delta S^\circ$ (kJ mol^{-1})	$\lvert\frac{10^2 T\Delta S^\circ}{\Delta G^\circ}\rvert$	Ref.
Pyrazole	2.61 ± 0.05	14.9 ± 0.3	14.7 ± 0.1	0.8	0.24	2	14
Imidazole	6.98 ± 0.02	39.9 ± 0.2	37.4 ± 2	8.4 ± 6	2.5	6	5
	6.993 ± 0.00	39.917 ± 0.004	36.79 ± 0.12	10.49 ± 0.41	3.13	8	24
1,2,4-Triazole	2.39 ± 0.02	13.6 ± 0.2	10.5 ± 3	10.5	3.1	23	This work
	2.45 ± 0.03	14.0 ± 0.2	9.62 ± 0.04	14.6	4.4	31	14

ΔG° in both cases. A similar difference between the two protonation equilibria is observed when inspecting the dependence of the $|10^2 T\Delta S^\circ/\Delta G^\circ|$ values on the number of the ring nitrogen atoms. Generally the entropy and enthalpy effects increase with the increasing number of the nitrogen atoms in the heterocycles for both protonation processes.

Spectrophotometric part. The ultraviolet and visible spectra have been frequently used in ionization studies of compounds (Ref. 13, pp. 65–108).[25–27] In the case of 1,2,4-triazole this is based on the changes in the intensity and place of the absorption of the $\pi \rightarrow \pi^*$ transitions with pH of the solutions. The light absorption of the solutions of 1,2,4-triazole may be assumed to depend on the species H_2L^+, HL, and L^- according to the equation:

$$A = \varepsilon C_{HL} = \varepsilon_{H_2L^+}[H_2L^+] + \varepsilon_{HL}[HL] + \varepsilon_{L^-}[L^-] \quad (14)$$

where $\varepsilon_{H_2L^+}$, ε_{HL} and ε_{L^-} are the absorptivities of the species, respectively. By taking into account eqns. (3) and (4) and the total concentration of 1,2,4-triazole it follows from eqn. (14) that [25]

$$(\varepsilon - \varepsilon_{HL}) + (\varepsilon - \varepsilon_{H_2L^+})[H^+]K_2 + (\varepsilon - \varepsilon_{L^-})/[H^+]K_1 = 0 \quad (15)$$

ε_{L^-} is obtained by measuring in strongly alkaline solutions and $\varepsilon_{H_2L^+}$ and ε_{HL} may be

Table 8. The wavelength, absorbance, and log ε values of the observed absorption maxima of 1,2,4-triazole in aqueous solutions at room temperature (~ 22 °C, 3×10^{-4} M) and 25 °C (2.996×10^{-4} M). The wavelength range 185–235 nm. The solution numbers refer to Fig. 4.

Room temperature (~ 22 °C)					25 °C				
Solution No.	pH	λ_{max} nm	A	log ε	Solution No.	pH	λ_{max} nm	A	log ε
1	1.09	189.5	0.565	3.275	1	1.09	189.6	0.616	3.313
2	2.11	189.5	0.660	3.342	2	2.08	189.6	0.678	3.355
3	3.05	189.5	0.710	3.374	3	3.01	189.6	0.807	3.430
4	6.05	189.5	0.745	3.395	4	6.40	189.5	0.845	3.450
5	8.01	190.0	0.600	3.301	5	7.88	189.8	0.762	3.405
6	10.02	197.0	0.520	3.239	6	9.89	195.6	0.741	3.393
7	12.14	209.0	0.040	2.125	7	11.97	–	–	–

Table 9. The wavelength and absorbance values of the observed absorption maxima of a compound X in 0.2 M aqueous solutions of 1,2,4-triazole at room temperature (~ 22 °C) and 25 °C. The wavelength range 220–290 nm. The solution numbers refer to Fig. 5.

Room temperature (~ 22 °C)				25 °C			
Solution No.	pH	λ_{max} nm	A	Solution No.	pH	λ_{max} nm	A
1	0.10	–	–	1	0.10	–	–
2	3.49	–	–	2	3.49	–	–
3	4.53	256	0.450	3	4.53	257.3	0.449
4	6.07	257	0.495	4	6.17	257.5	0.493
6	8.68	257	0.485	5	7.85	257.5	0.492
7	13.90	257	0.495	6	8.66	257.5	0.499
Isosbestic	point	248	0.360	7	13.73	257.5	0.497
				Isosbestic	point	248.5	0.371

measured or calculated in strongly acid and nearly neutral solutions of 1,2,4-triazole, respectively.

The position, absorbance, and log ε values of the absorption maxima observed in the spectra of 1,2,4-triazole in aqueous solutions in the range 185–235 nm are given in Tables 8 and 10 and in ethanol and hexane solutions in Table 11. The wavelengths and log ε values for the absorption maxima of the different species of 1,2,4-triazole in aqueous solutions recorded or calculated from eqn. (15) are represented in Table 12. The absorption spectra of 1,2,4-triazole in different solutions are shown in Figs. 4 and 6. The corresponding data for the compound X discussed later are given in Tables 9 and 11 and in Figs. 5 and 6.

When considering the recorded absorption spectra of 1,2,4-triazole, (Figs. 4–6 and Tables 8–12) two separate absorption maxima are observed. The strong maximum (A) at a shorter wavelength corresponds to an allowed transition $\pi - \pi^*$ (Ref. 7, p. 17; Ref. 26, pp. 129 and 144); whereas (B) at a longer wavelength is obviously due to corresponding electron transitions of an unknown compound X. Generally the position of the maximum B is almost constant in water ($\lambda_{max} = 257.5$ nm) and ethanol ($\lambda_{max} = 258.6$ nm) solutions at 25 °C, while in acid solutions (Fig. 5) this maximum is transferred to shorter wavelengths, weakened and finally almost disappears. On the other hand the position of the absorption maximum A varies considerably. In acid and neutral water solutions it is at about 190 nm (Fig. 4). In alkaline solutions it can change to 210 nm (Fig. 4). In ethanol, which is not as polar a solvent as water, it exists in the range 201–206 nm ($\varepsilon = 475 - 112$) and in the nonpolar hexane at 196 nm (Fig. 6).

Table 10. The wavelength, absorbance, and log ε values of the observed absorption maximum of 1,2,4-triazole in different molar concentrations in water at 25 °C. The wavelength range 185–210 nm.

1,2,4-Triazole 10^4 mol l^{-1}	λ_{max} nm	A	log ε
2.996	189.5	0.845	3.450
1.498	189.5	0.431	3.459
0.7488	189.4	0.213	3.454
			Mean 3.454

By examining the absorptivities of the absorption maxima the Lambert-Beer law is found to hold for the A band in water solutions. In ethanol solutions this is not the case, since both λ_{max} and ε are changed with the concentration of 1,2,4-triazole, the ε values being lower in the latter solutions. In strongly alkaline solutions the A band seems to have disappeared. For the A band $\varepsilon_{H_3L^+} < \varepsilon_{HL}$. In the case of the B band we cannot say with certainty if the Lambert-Beer law holds in water and ethanol solutions. The absorptivity values are almost the same in the different solvents. In water solutions the B band seems to show the compound X to have two absorbing species.

Table 11. The wavelength, absorbance, and log ε values of the observed absorption maxima of a compound X and 1,2,4-triazole in ethanol and hexane solutions at room temperature (~ 22 °C) and 25 °C. The wavelength range 190–315 nm. The solution numbers refer to Fig. 6.

Room temperature (~ 22 °C)					25 °C				
Solution No.	1,2,4-Triazole 10^3 mol l^{-1}	λ_{max} nm	A	log ε	Solution No.	1,2,4-Triazole 10^3 mol l^{-1}	λ_{max} nm	A	log ε
3	80.0	258.5	0.205	—	1	198.9	258.6	0.475	
4	48.0	258.5	0.125	—	2	99.46	258.6	0.239	
5	28.8	258.5	0.075	—	3	79.57	258.6	0.187	
6	17.3	258.0	0.045	—	8	6.188	203.8	1.60	2.413
		207.5	1.365	1.897	10	2.228	202.1	0.882	2.598
7	10.4	257.5	0.030	—	11	1.337	201.7	0.592	2.646
		206.5	1.165	2.049	12	0.8019	201.4	0.381	2.677
8	6.22	205.0	0.970	2.193	13	satd.			
9	3.73	204.0	0.750	2.303		hexane	196.0	0.095	—
10	2.24	203.5	0.535	2.378					
11	1.34	203.0	0.360	2.429					

Rao (Ref. 7, p. 77) and Mason [28] collected and compared the absorption spectra of many unsaturated five-membered heterocycles found in the literature. The strong absorption maxima at the range 207–210 nm found in the spectra of pyrazole, imidazole, and 1,2,3-triazole in alcoholic solutions are obviously due to $\pi \rightarrow \pi^*$ excitations in C=C or C=N bonds. The A band in the absorption spectrum of 1,2,4-triazole is also obviously of the same origin, owing to $\pi \rightarrow \pi^*$ transitions in C=N bonds.

Previously Mason [28] obtained for λ_{max} and ε of 1,2,4-triazole in water the values 187 nm and 3300, respectively. The experimental conditions were not specified in greater detail. In the present work we obtained in an unbuffered water solution at 25 °C $\lambda_{max} = 189.5$ nm and $\varepsilon = 2850$.

A closer inspection of the absorption band A in acid solutions (Fig. 4) shows a shoulder on the longer wavelength side of the maximum. When pH of the solution is increased, a shoulder also appears on the shorter wavelength side of the absorption. At pH about 8, two very close peaks are observed at the maximum, and when the spectrum is nearest to that of the HL species. In alkaline solutions this absorption band is transformed to longer wavelengths and weakened considerably or disappears.

There are several possibilities to be considered as a possible explanation of the observed shoulders and the double peak. The most probable explanation of the appearance and disappearance of the shoulders and the double peak in the band A is, however, the tautomeric equilibrium between 1*H*-1,2,4- and 4*H*-1,2,4-triazole which shifts with the pH of the solution. The shoulder and the stronger peak on the shorter wavelength side are probably due to 1*H*-1,2,4-triazole, and the other shoulder and peak arise from 4*H*-1,2,4-triazole according to their shown tautomeric ratio [3] (5–10:1). The observed double peak in the absorption spectrum of 3,5-diphenyl-1,2,4-triazole at 230–270 nm has previously been assumed to arise from the 1*H*-1,2,4- and 4*H*-1,2,4-triazole tautomerism,[29] but in reverse order.

The absorption band B (Fig. 5) is obviously due to the $\pi \rightarrow \pi^*$ excitations in a compound X, and should not be taken to be a band of a weak forbidden $n \rightarrow \pi^*$ transition in 1,2,4-triazole (Table 9). It should be mentioned that an absorption band B has not been observed in the spectrum of 1,2,3-triazole (Ref. 7, p. 77). It is reported to have been observed, however, in the spectrum of imidazole (Ref. 7, p. 77).

Table 12. The wavelength and log ε values of the absorption maxima of the different species of 1,2,4-triazole in aqueous solutions at 25 °C.

Species	λ_{max} (nm)	log ε
H_2L^+	189.6	3.308
HL	189.5	3.441

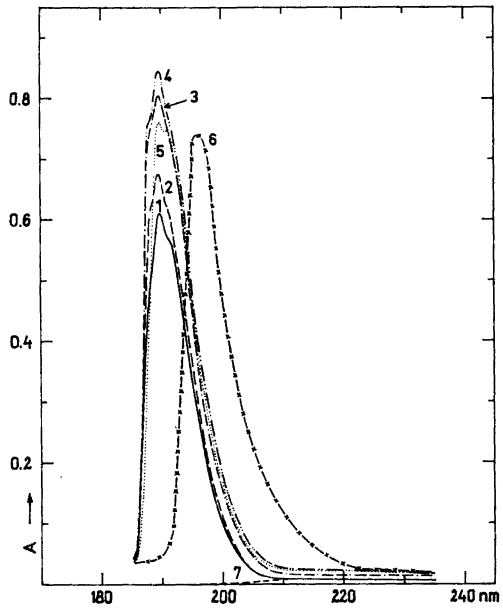

Fig. 4. The absorption spectra of 2.996×10^{-4} M aqueous solutions of 1,2,4-triazole at 25 °C. The wavelength range 185–235 nm.

Curve No.	pH	$C \times 10^4$	$C_B \times 10^4$
$HClO_4$			
1	1.09	992.4	
2	2.08	99.9	
3	3.01	9.99	
4	6.40	–	
H_3BO_3			
5	7.88	499.4	39.65
6	9.89	499.4	438.5
7	11.97	–	99.9

The values $\lambda_{max} = 260$ nm and $\varepsilon < 5$ were given for the $n \rightarrow \pi^*$ transition in tetrazole (Ref. 7, p. 77).

Atkinson *et al.*[29] have concluded that 1,2,4-triazole and its alkyl derivatives would not have an absorption spectrum at longer wavelengths than 215 nm. Also Mason [28] has not observed such a one. The measurements in the present work confirmed these results, as will be shown in the following.

From the following facts it can be concluded that in the case of the B band it is a band caused by an unknown compound X, present in 1,2,4-triazole, and not a band of a weak forbidden $n \rightarrow \pi^*$ excitation in 1,2,4-triazole.

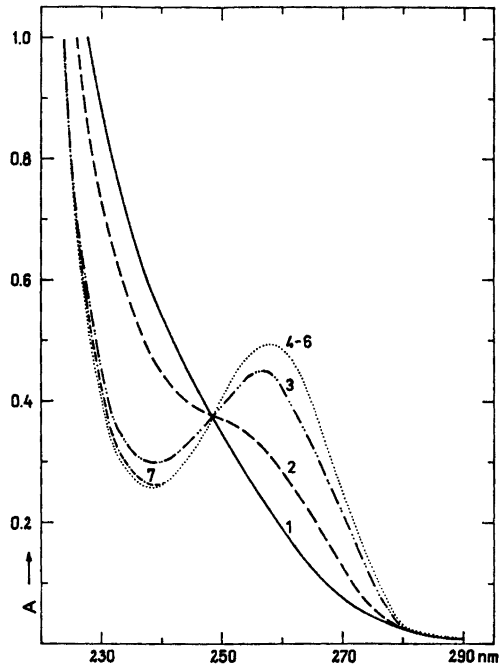

Fig. 5. The absorptin spectra of a compound X in 0.1998 M aqueous solutions of 1,2,4-triazole at 25 °C. The wavelength range 220–290 nm.

Curve No.	pH	$C \times 10^4$ HCl	$C_{NaCl} \times 10^4$	$C_B \times 10^4$
1	0.10	9940	–	–
2	3.49	–	100	–
3	4.53	10	190	–
4	6.17	–	200	–
5	7.85	– [a]	100	39.7
6	8.66	–	100	100
7	13.73	–	–	9990

[a] $C_{H_3BO_3} \times 10^4 = 500$.

The band at about 258 nm does not show the blue shift typical for a forbidden $n \rightarrow \pi^*$ band when transforming from a nonpolar solvent, hexane, to polar solvents, ethanol and water.[30,31]

The absorptivity of a neutral solution, 2.996×10^{-4} M in 1,2,4-triazole (Fig. 4) is about 0.03 at 230 nm. In a similar solution, 0.1998 M in 1,2,4-triazole it should be, accordingly, about 20. In Fig. 5, however, the absorbance value is seen to be about 0.4 only.

Solution No.	λ	A	C_{HL}	pH	$[H^+]$	A_{HL}	$A_{H_2L^+}$	$\log K_2$	I
2	189.6	0.678	2.996×10^{-4}	2.08	8.32×10^{-3}	0.845	0.609	2.46	0.01
3	189.6	0.807	2.996×10^{-4}	3.01	9.78×10^{-4}	0.845	0.609	2.29	0.001
2	240	0.448	0.1998	3.49	3.24×10^{-4}	0.263	0.538	3.80	0.02
2	257.3	0.320	0.1998	3.49	3.24×10^{-4}	0.495	0.233	3.79	0.02
3	240	0.298	0.1998	4.53	2.95×10^{-5}	0.263	0.538	3.69	0.02
3	257.3	0.449	0.1998	4.53	2.95×10^{-5}	0.495	0.233	3.86	0.02
Solution No.						4	1		

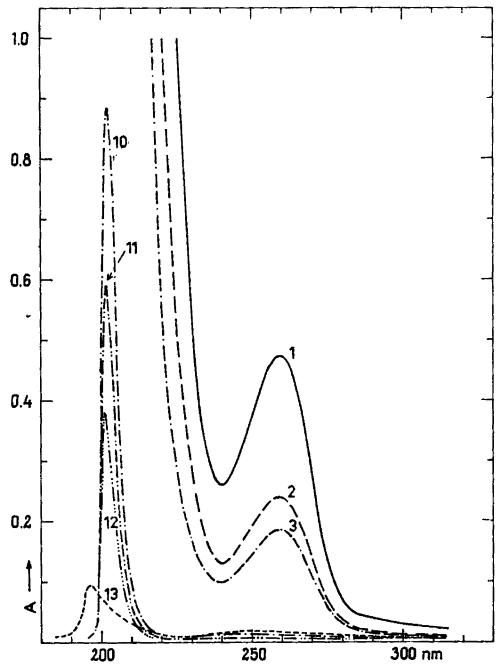

Fig. 6. The absorption spectra of a compound X and 1,2,4-triazole in ethanol and hexane solutions at 25 °C. The wavelength range 180–320 nm.

Curve No.	[1,2,4-Triazole] M
1	0.1989
2	0.09946
3	0.07957
10	2.228×10^{-3}
11	1.337×10^{-3}
12	8.019×10^{-4}
13	[a]

[a] Saturated solution of 1,2,4-triazole in hexane (20 °C).

If the 1,2,4-triazole used contains, as our analysis indicates, about 0.4 % of a compound X, this means that a 0.2 M 1,2,4-triazole solution would be about 8×10^{-4} M in the compound X (Figs. 5 and 6). This concentration is of the usual order of magnitude used in spectral studies of protonable compounds showing absorption at 240–400 nm.[25]

If we evaluate the protonation constants which it is possible to calculate from the absorption spectra presented in Figs. 4 and 5 at the band maxima and 240 nm using eqn. (15) we obtain the above results at 25 °C.

So we get at 189.6 nm for $\log K_2$ of 1,2,4-triazole as a mean value 2.38 in excellent agreement with Fig. 2. Instead of that in the range 240–260 nm we get 3.79 as a mean for $\log K_2$, which implies that we are dealing with some unknown compound X in place of 1,2,4-triazole. The result is the same, if the compound X is assumed to protonize according to eqn. (1) in lieu of eqn. (2) when using eqn. (15) to evaluate the protonation constant. This result and the spectra in Fig. 5 which show only one isosbestic point (248.5 nm) and that the compound X probably has only two species in water from strongly alkaline to strongly acidic solutions, confirm the above-made conclusion on the origin of band B.

Two times higher absorbances showed by 1,2,4-triazole produced by Light & Koch in similar conditions under which spectra Nos. 1–3 in Fig. 5 and spectrum No. 2 in Fig. 6 were taken, implied that this product contains about two times more of the compound X than the product of EGA-Chemie. The product did not dissolve completely, but showed an opalescence.

The present results also cast doubt on all reported weak bands said to be due to forbid-

den $n \rightarrow \pi^*$ transitions the ε values of which are ≤ 100. Examples are imidazole and tetrazole mentioned above (Ref. 7, p. 77). In any case the origin of the band, *i.e.* whether it is due to the true compound or some minor impurity, should be tested by evaluation of the protonation constants, if the compound has such, from the absorption spectra in aqueous solutions, and by comparing the results with, in some other way determined, known values of the constants. This seems to be a generally acceptable method and should be used to ascertain the source of the spectrum. In no case one should be satisfied with absorption measurements in nonpolar solvents only. In this respect, compare the spectra in Figs. 5 and 6.

The studies of the solvent effects were limited mostly to water and ethanol, because of the insolubility of 1,2,4-triazole. Hexane and heptane, the absorption of which is not disturbing in the wavelength range in question were wholly or almost unsuitable for this reason also. The polar-nonpolar effect of the solvents (a red shift) on the absorption spectrum of 1,2,4-triazole, in accordance with what was said above, is clearly observed to respond to the band due to the $\pi \rightarrow \pi^*$ transition in the wavelength range 180 – 240 nm (Fig. 6).

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