glacial acetic acid. *p*-Methoxybutyrophenone was made from the *p*-hydroxy compound and methyl iodide in the presence of sodium hydroxide and was purified by vacuum distillation. Valerophenone, 1-phenyl-4-methylpentan-1-one, and *p*-chlorobutyrophenone were prepared from the corresponding benzaldehyde and alkylmagnesium bromide by oxidation of the first-formed substituted benzyl alcohol. Typically, benzaldehyde (0.17 mole) in ether (20 ml) was added slowly to *n*-butylmagnesium bromide (0.20 mole) in ether (100 ml), and the mixture was refluxed for 30 min, then hydrolyzed with ice and concentrated hydrochloric acid. The 1-phenylpentan-1-ol was extracted with ether, and the crude product was oxidized by warming to 65° for 6 hr with acidified potassium dichromate solution. The product was extracted with ether, and the crude ketone was purified by vacuum distillation. The over-all yields were in the range 50–75%.

Ultraviolet spectra were recorded on a Unicam SP800 spectrometer, phosphorescence spectra on an Aminco-Bowman spectrofluorometer with phosphoroscope, and mass spectra on an AEI MS9 instrument. The glasses used for phosphorescence were 1:5 methylcyclohexane:isopentane or 2:1 methylcyclohexane:*n*-hexane (nonpolar), and 2:1 ethanol:ether, 1:1 ethanol:methanol, or 5:5:2 ether:isopentane:ethanol (polar).

Irradiations. Large-scale irradiations were carried out in a reactor with a centrally placed 450-W medium-pressure mercury lamp. The acetophenone and cyclobutanol products were isolated by preparative vpc on a column of 30% Perkin-Elmer Silicon Fluid FS1265 on "Anakrom", 40–50 Å. The structures of acetophenone itself, *p*-chloroacetophenone, *p*-methoxyacetophenone, 1-phenylcyclobutanol, and 2-methyl-1-phenylcyclobutanol were confirmed by analysis and by infrared, nmr, and mass spectra.

2,2-Dimethyl-1-phenylcyclobutanol was isolated as a colorless oil. *Anal.* Calcd for $C_{12}H_{16}O$: C, 81.8; H, 9.1. Found: C, 81.7; H, 9.0. Infrared showed no carbonyl absorption, and nmr showed a signal at τ 7.54 (CCl_4) which was reduced with D_2O. The cyclobutanol from *p*-chlorobutyrophenone could not be isolated by this method nor could it be satisfactorily isolated by column chromatography on silica gel.

From the product of the irradiation of butyrophenone in acetonitrile dibenzoylethane was isolated as colorless crystals by chromatography on a column of silica gel with chloroform as eluent. This compound was recognized by its melting point (139–140°) and by its simple infrared, nmr, and mass spectra.

Comparative experiments were carried out in a roundabout apparatus having 12 equally spaced quartz reaction tubes suspended vertically near the outer rim of a metal disk; this disk rotates about the vertical axis through its center. The lamp, contained in a water-cooled Pyrex probe, was positioned to lie along the axis. A filter solution containing potassium chromate (0.002 *M*) and potassium carbonate (0.05 *M*) in water, and of path length 4.8 mm, was used to isolate the 313-nm region. The ketone solutions were about 0.15 *M*, and the product solutions were analyzed by vpc on a column of Perkin-Elmer Silicone Fluid FS1265, with a detector of the hydrogen flame combustion type, the response of which was known from calibration against the pure compounds. The reactions were not allowed to proceed beyond 10% conversion, and in some cases *m*-dichlorobenzene was used as an internal standard.

To investigate the reaction at different temperatures, the large-scale apparatus was used in a water bath maintained at a constant temperature, and for each measurement the conditions other than temperature were as nearly as possible identical. In order to obtain reliable results, conversions of more than 10% were necessary in most of these runs.

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Thermodynamics of Proton Ionization from Some Substituted 1,2,3-Triazoles in Dilute Aqueous Solution

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Abstract: $\Delta H°$, $\Delta S°$, and p*K* values valid at 25° and zero ionic strength are reported for 1,2,3-triazole, 4,5-dibromo-1,2,3-triazole, 1,2,3-triazole-4-carboxylic acid, 1,2,3-triazole-4,5-dicarboxylic acid, benzotriazole, 1-phenyl-1,2,3-triazole-4-carboxylic acid, 1-phenyl-1,2,3-triazole-4,5-dicarboxylic acid, and 1-phenyl-5-methyl-1,2,3-triazole-4-carboxylic acid. Unusual substitution effects on the thermodynamics of proton ionization from the triazole ring are found.

A study of proton ionization from the 1,2,3-triazole ring is of interest for several reasons: (a) it is isoelectronic with the biologically important imidazole ring, (b) the bond structure of the ring is as yet poorly known, (c) the change in acidity of 1,2,3-triazoles do not seem to follow the same pattern with substitution as more familiar acid groups do, and (d) very little thermodynamic data were previously available on this system.

No ΔH values have previously been reported for proton ionization from 1,2,3-triazoles, and the only p*K* values reported for the compounds included in this study are those for triazole[1] and benzotriazole.[1] The purpose of this study was to determine the effects of substituents on the $\Delta H°$, $\Delta S°$, and p*K* values for proton ionization from the 1,2,3-triazole ring.

Experimental Section

Materials and Equipment. Compounds used for this study were prepared by known methods,[2] and the structures were verified either from the synthesis procedure or by proton nuclear magnetic resonance spectra. Equivalent weight determinations by titration

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(1) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworth & Co. (Publishers), Ltd., London, 1965.

(2) (a) 1,2,3-Triazole: O. Dimroth and G. Fester, *Ber.*, 43, 2222 (1910); (b) 1,2,3-triazole-4-carboxylic acid: E. Oliveri-Mandala and A. Coppola, *Gazz. Chim. Ital.*, [II] 40, 436 (1910); (c) 1,2,3-triazole-4,5-dicarboxylic acid: J. Bladin, *Ber.*, **26**, 545 (1893) (subsequently treated with strongly acidic cation-exchange resin to remove the K^+); (d) benzotriazole: Eastman, Practical grade, crystallized from EtOH and then from H_2O; (e) 4,5-dibromo-1,2,3-triazole: R. Huttel and A. Gebhardt, *Ann.*, **558**, 34 (1947); (f) 1-phenyl-1,2,3-triazole-4,5-dicarboxylic acid, 1-phenyl-5-methyl-1,2,3-triazole-4-carboxylic acid, and 1-phenyl-1,2,3-triazole-4-carboxylic acid: O. Dimroth, *Ber.*, **35**, 1029 (1902).

with NaOH solution showed all of the compounds used in this study to be 99+% pure except for 1-phenyl-1,2,3-triazole-4,5-dicarboxylic acid, which was found to crystallize as a hemihydrate.

Sodium hydroxide solutions were prepared from carbonate-free 50% Baker Analyzed reagent grade solutions and were standardized with NBS potassium acid phthalate acidimetric standard. Buffer solutions used for the standardization of the pH meter were pH 4.004 (potassium acid phthalate) and 6.865 (phosphate) buffers prepared from NBS instructions and materials. Perchloric acid solutions were prepared from Baker Analyzed reagent grade 70% perchloric acid solution. The water used for all experiments was double distilled and boiled just previous to use. All solutions were stored in bottles equipped with Ascarite tubes and were subsequently used under an atmosphere of pure nitrogen. A Beckman research model pH meter equipped with a Beckman E-3 glass electrode and a saturated calomel electrode was used for the pH measurements.

The calorimeter employed was a 180-ml, thin-wall, cylindrical dewar flask immersed in a constant-temperature bath. The constant-temperature bath was controlled to ±0.001° by a Hallikainen Instruments Corp. Resistitrol. This bath was immersed in a larger bath whose temperature was controlled to ±0.05° by a Thermistemp Model 71 temperature controller. The stirrer in the dewar was driven by a 600-rpm synchronous motor. The temperature-sensing device for the dewar consisted of a 5000-ohm Veco thermistor which was one leg of a Wheatstone bridge, powdered by a 1.5000-V dc source. A Sargent Model SR 1-mV recorder was used to follow the unbalance potential from the bridge, and the auxiliary emf from a Leeds and Northrup K-3 potentiometer was used to furnish a bucking potential. The unbalance potential of the bridge was calibrated against a 1° Beckman thermometer manufactured by H. B. Instrument Co. and calibrated by NBS. The 13.04-cal/mV sensitivity of the calorimeter was increased by the addition of a Leeds and Northrup Model 9835 dc preamplifier. The heater circuit used for the determination of the heat capacity of the calorimeter was a conventional circuit powered with a 12-V battery. The heater was 20 ohms of Karma wire, coiled and encapsulated in epoxy, and the standard resistor was an 8-ohm, 250-W resistor which was periodically calibrated against a 10-ohm NBS certified standard. The timer used was accurate to ±0.05 sec.

The device for mixing the two solutions inside the dewar consisted of a 5-ml capsule made from the barrel of a polypropylene syringe and stoppered at either end with two rubber plugs from two other identical syringes. A nylon rod was used to push the plugs from the capsule. By doing blank experiments with water in both containers, it was found that opening the capsule produced 0.107 ± 0.017 cal where the deviation is the average deviation for 12 determinations.

The accuracy of the calorimeter was checked by determining ΔH_i for H_2O. A value of 13.35 ± 0.05 kcal/mole was found, which is in good agreement with earlier values.[3]

Procedure. For the pK determinations, solutions of the triazoles were titrated with a standard solution of NaOH. Several titrations were carried out for each compound, and several pH measurements were taken in each buffer region.

For the ΔH determinations, solutions of the sodium salts of the triazoles were prepared by adding slightly less than an equivalent amount of standard NaOH solution to a solution of the acid; these solutions were allowed to react with $HClO_4$ solution in the calorimeter. The stronger acids (p$K < 2$) were treated directly without conversion to the sodium salt. The total volume of solution in the calorimeter was 179.7 ml.

Calculations

The method used for the calculation of pK values has been described.[4] An IBM 650 computer was used to do the calculations. Because of the low solubility of most of the compounds studied, the pK values were determined at a single, low ionic strength and extrapolated to $\mu = 0$ using activity coefficients calculated from the extended Debye–Hückel equation with $a = 5$ Å. Since the ΔH determinations were done at an ionic strength, μ, less than 0.05, it was assumed that $\Delta H^{\mu} = \Delta H^{\circ}$. The standard state used in this study is defined to be an ideal 1 M solution.

The deviations for pK values reported in Table III are average deviations from the mean and represent the average deviation between runs. The average deviation between values obtained in any single run were all less than ±0.005 pK unit.

The ΔH values were computed from the measured heat changes, corrected for the heat of dilution of perchloric acid and the heat of ionization of water, and from calculated species distributions (Table I).

Table I. Data for ΔH Determinations

Solution in dewar (174.7 ml)		$[HClO_4]$ in capsule				
[NaOH], mM	[Compound], mM	(4.97 ml), mM	q_{meas},[a] cal	q_{corr}[b] cal	q_{H_2O},[c] cal	Δn,[d] mmoles
Benzotriazole						
7.95	8.44	41.3_7	1.53_8	1.54_3	0.059	0.2014
7.95	8.44	41.3_7	1.56_4	1.56_9	0.059	0.2014
7.95	8.44	41.3_7	1.56_5	1.57_0	0.059	0.2014
7.95	8.44	41.3_7	1.56_5	1.57_0	0.059	0.2014
1,2,3-Triazole						
3.84	7.04	41.3_7	1.82_5	1.83_2	0.024	0.2040
3.84	7.04	41.3_7	1.82_5	1.83_2	0.024	0.2040
3.84	7.04	41.3_7	1.83_8	1.84_5	0.024	0.2040
4,5-Dibromo-1,2,3-triazole						
3.84	4.65	41.3_7	0.86_0	0.86_7	0.000	0.2050
3.84	4.65	41.3_7	0.88_7	0.89_3	0.000	0.2050
3.84	4.65	41.3_7	0.84_7	0.85_4	0.000	0.2050
3.84	4.65	41.3_7	0.86_0	0.86_8	0.000	0.2050
1-Phenyl-5-methyl-1,2,3-triazole-4-carboxylic Acid						
2.24	3.77	41.3_7	0.02_0	0.02_8	0.000	0.1753
2.24	3.77	41.3_7	0.00_3	0.01_1	0.000	0.1753
2.24	3.77	41.3_7	0.04_3	0.05_0	0.000	0.1753
1-Phenyl-1,2,3-triazole-4-carboxylic Acid						
0.795	1.305	41.3_7	0.01_7	0.02_6	0.000	0.0596
0.795	1.305	41.3_7	0.04_2	0.05_0	0.000	0.0596
0.795	1.305	41.3_7	0.05_2	0.06_1	0.000	0.0596
1-Phenyl-1,2,3-triazole-4,5-dicarboxylic Acid						
0	1.519	102.6	0.37_8	-0.10_5	0.000	0.1578
0	1.519	102.6	0.45_6	-0.10_5	0.000	0.1578
2.197	1.265	41.3_7	0.00_0	0.00_9	0.000	0.1610
2.197	1.265	41.3_7	0.00_0	0.00_9	0.000	0.1610
1,2,3-Triazole-4-carboxylic Acid						
0.000	2.676	41.3_7	0.05_3	0.06_1	0.000	0.0575
0.000	2.676	41.3_7	0.02_6	0.03_5	0.000	0.0575
4.503	2.520	41.3_7	1.21_6	1.22_3	0.034_3	0.2015
4.503	2.520	41.3_7	1.26_5	1.27_2	0.034_3	0.2015
4.503	2.520	41.3_7	1.26_5	1.27_2	0.034_3	0.2015

[a] q_{meas} = measured calories corrected for stirring energy, heat produced from capsule opening, and all other nonchemical effects. [b] $q_{cor} = q_{meas} - q_{dil}$, where the heat of dilution, q_{dil}, was calculated from data in V. B. Parker, "Thermal Properties of Aqueous, Univalent Electrolytes," National Standard Reference Data Series, National Bureau of Standards, U. S. Government Printing Office, Washington, D. C., 1965. [c] ΔH_i for H_2O was taken to be 13.36 kcal/mole at all ionic strengths used in this study. [d] Δn = the number of millimoles of acid anion protonated in the calorimeter and was calculated using the pK values determined in this study.

Deviations for values of ΔH given in Table III are average deviations from the mean. For the diprotic acids, all possible combinations between runs for the first and second proton ionization were used in arriving

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(3) (a) J. D. Hale, R. M. Izatt, and J. J. Christensen, *J. Phys. Chem.*, 67, 2605 (1963); (b) C. E. Vanderzee and J. A. Swanson, *ibid.*, 67, 2608 (1963).

(4) L. D. Hansen, J. A. Partridge, R. M. Izatt, and J. J. Christensen, *Inorg. Chem.*, **5**, 569 (1966).

Table II. Sample Data for pK Determinations[a,b]

1,2,3-Triazole (9) (49.91 ml of 4.72 m*M*)											
pH	8.633	8.784	8.874	8.953	9.030	9.100	9.167	9.213	9.306	9.374	
ml	0.966	1.272	1.471	1.670	1.871	2.071	2.271	2.471	2.671	2.871	
Benzotriazole (5) (49.91 ml of 4.27 m*M*)											
pH	7.844	7.948	8.040	8.126	8.206	8.278	8.357	8.424	8.496		
ml	0.995	1.200	1.395	1.610	1.812	2.000	2.400	2.599	2.805		
4,5-Dibromo-1,2,3-triazole (5) (49.91 ml of 3.68 m*M*)											
pH	4.892	4.974	5.076	5.182	5.240	5.324	5.411	5.500	5.593	5.696	5.798
ml	0.850	1.049	1.250	1.451	1.640	1.845	2.045	2.351	2.452	2.650	2.842
1-Phenyl-5-methyl-1,2,3-triazole-4-carboxylic Acid (5) (99.80 ml of 1.087 m*M*)											
pH	3.486	3.526	3.574	3.620	3.692	3.763	3.830	3.915	3.986	4.098	4.290
ml	0.121	0.231	0.375	0.486	0.675	0.830	0.980	1.135	1.278	1.437	1.685
1-Phenyl-1,2,3-triazole-4-carboxylic Acid (4) (99.80 ml of 0.831 m*M*)											
pH	3.261	3.289	3.318	3.353	3.394	3.436	3.478				
ml	0.070	0.160	0.259	0.360	0.467	0.573	0.670				
1-Phenyl-1,2,3-triazole-4,5-dicarboxylic Acid (2) (49.91 ml of 2.978 m*M*)											
pH	2.850	2.926	2.990	3.090	3.181	3.256	3.358	3.442			
ml	1.113	1.443	1.678	1.963	2.202	2.342	2.533	2.673			
pH	3.580	3.688	3.826	3.946	4.027	4.105	4.180	4.250			
ml	2.863	3.007	3.153	3.293	3.383	3.481	3.578	3.673			
pH	4.328	4.410	4.478	4.568	4.605	4.720	4.780				
ml	3.765	3.913	4.007	4.163	4.253	4.441	4.533				
pH	4.846	4.913	4.976	5.026	5.096	5.176	5.250	5.320	5.396		
ml	4.629	4.773	4.918	5.013	5.108	5.203	5.293	5.393	5.490		
pH	5.498	5.602	5.750	5.974	6.326	6.621					
ml	5.583	5.685	5.773	5.873	5.964	6.013					
1,2,3-Triazole-4-carboxylic Acid (6) (49.91 ml of 2.35_5 m*M*)											
pH	3.145	3.214	3.280	3.346	3.414	3.490	3.572				
ml	0.162	0.367	0.657	0.865	1.065	1.265	1.465				
pH	3.690	3.832	4.020	4.750	8.000	8.099	8.164				
ml	1.666	1.865	2.065	2.764	2.965	3.064	3.160				
pH	8.215	8.293	8.436	8.510	8.621	8.692	8.773	8.883			
ml	3.215	3.327	3.534	3.645	3.797	3.915	4.035	4.194			
1,2,3-Triazole-4,5-dicarboxylic Acid (3) (49.91 ml of 2.42_6 m*M*)											
pH	2.747	2.785	2.830	2.898	2.958	3.020	3.096	3.182	3.293	3.436	
ml	0.180	0.376	0.590	0.890	1.089	1.285	1.491	1.690	1.889	2.080	
pH	3.526	3.584	3.658	3.822	4.055	4.376	4.670	4.870	5.040	5.276	
ml	2.175	2.229	2.289	2.390	2.490	2.592	2.691	2.790	2.890	3.090	
pH	5.482	5.682	5.828	5.908	5.962	6.045	6.101	6.193	6.333	6.608	
ml	3.320	3.590	3.825	3.938	4.055	4.145	4.230	4.360	4.535	4.796	
pH	6.896	7.106	7.420	7.801	8.100	8.390	8.610	8.701	8.851		
ml	4.977	5.057	5.147	5.249	5.367	5.549	5.768	5.867	6.062		
pH	8.983	9.048	9.147	9.273	9.441	9.603	9.772	9.976			
ml	6.263	6.367	6.518	6.712	6.967	7.167	7.367	7.563			

[a] ml column refers to milliliters of 0.0475 *M* NaOH solution added. [b] Number in parentheses following each compound refers to the total number of pH titrations made on that compound.

at an average value of $\Delta H_1°$ and $\Delta H_2°$. For each of the diprotic acids, the first two runs listed are for the first proton and the remaining runs listed are for the second proton.

For the method used in determining the $\Delta H°$ values for the triprotic acid, refer to footnotes *a* and *b* of Table III.

Results

The data from which the ΔH values were calculated are given in Table I. A sample of the data from which the p*K* values were calculated is given in Table II for each compound. The average p*K*, $\Delta H°$, and $\Delta S°$ values are compiled in Table III. The limits of error are expressed as average deviations from the mean.

The agreement of the pK_1 value (Table III) for 1,2,3-triazole-4,5-dicarboxylic acid which was determined with a pH meter (1.86 ± 0.08) with the value which was independently determined by the entropy titration method (1.94 ± 0.04) clearly shows that no sizable systematic errors exist in our measurements or the relatively small p*K* values encountered in this study.

Discussion

In previous studies of the thermodynamics of proton ionization from carboxyl groups, it has been found that the magnitude of the free-energy change or p*K* is determined primarily by the entropy change.[5] The enthalpy change is nearly always near zero for proton ionization from substituted carboxyl groups. This same result is found for the ionization of a carboxyl group in the 1,2,3-triazolecarboxylic acids. In contrast, the data in Table III show that the enthalpy change for ionization from the N–H group in the

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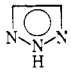
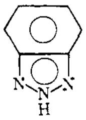
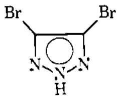
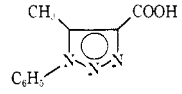
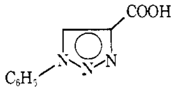
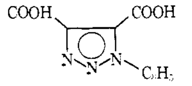
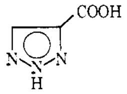
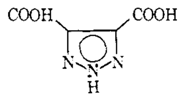
[5] J. J. Christensen, R. M. Izatt, and L. D. Hansen, *J. Am. Chem. Soc.*, **89**, 213 (1967).

Table III. pK, $\Delta H°$, and $\Delta S°$ Values for Proton Ionization from Some Substituted 1,2,3-Triazoles

Acid	Structure	pK	$\Delta H°$, kcal/mole	$\Delta S°$, gibbs/mole
1,2,3-Triazole		9.26 ± 0.02 $(9.51)^a$	$+8.88 \pm 0.03$	-12.6
Benzotriazole		8.38 ± 0.03 $(8.64)^a$	$+7.47 \pm 0.05$	-13.3
4,5-Dibromo-1,2,3-triazole		5.37 ± 0.06	$+4.24 \pm 0.06$	-10.4
1-Phenyl-5-methyl-1,2,3-triazole-4-carboxylic acid		3.73 ± 0.06	$+0.17 \pm 0.08$	-16.5
1-Phenyl-1,2,3-triazole-4-carboxylic acid		2.88 ± 0.06	$+0.76 \pm 0.26$	-10.6
1-Phenyl-1,2,3-triazole-4,5-dicarboxylic acid		p$K_1 = 2.13 \pm 0.17$ p$K_2 = 4.93 \pm 0.03$	-0.67 ± 0.23 $+0.06 \pm 0.05$	-11.1 -22.3
1,2,3-Triazole-4-carboxylic acid		p$K_1 = 3.22 \pm 0.09$ p$K_2 = 8.73 \pm 0.14$	$+0.84 \pm 0.20$ $+5.89 \pm 0.10$	-11.5 -20.2
1,2,3-Triazole-4,5-dicarboxylic acid		p$K_1 = 1.86 \pm 0.08$ $(1.94 \pm 0.04)^b$ p$K_2 = 5.90 \pm 0.05$ p$K_3 = 9.30 \pm 0.05$	$+0.11 \pm 0.05^b$ $+0.01 \pm 0.05^c$ $+2.26 \pm 0.05^c$	-8.2 -27.0 -35.0

[a] See ref 1. [b] These values were determined using an "entropy titration" procedure: J. J. Christensen, R. M. Izatt, L. D. Hansen, and J. A. Partridge, *J. Phys. Chem.*, **70**, 2003 (1966). The calorimeter used was a thermometric titration calorimeter which has been described by J. J. Christensen, R. M. Izatt, and L. D. Hansen, *Rev. Sci. Instr.*, **36**, 779 (1965). [c] The same calorimeter described in footnote *a* was used, but the ordinary calculation procedure [J. J. Christensen, R. M. Izatt, and L. D. Hansen, *J. Am. Chem. Soc.*, **89**, 213 (1967)] was used.

triazole ring is greatly affected by the nature of the group or groups substituted on the ring in the 4 and 5 positions. For example, ΔH for proton ionization from the NH group in the dianion of 1,2,3-triazole-4,5-dicarboxylic acid is 6.62 kcal/mole less positive than ΔH for proton ionization from 1,2,3-triazole itself. Thus, it is a curious fact that while the substituents on the ring produce large changes in the proton ionization properties of the ring, the ring in turn causes little or no change in the proton ionization properties of the substituent carboxyl group.

Any mechanism which describes the substituent effects on the thermodynamics of proton ionization from the NH group in 1,2,3-triazoles must be compatible with the above observations. The fact that the enthalpy change for the ionization from the carboxyl groups is the same regardless of the nature of the substituents can only be explained by assuming that the protonated carboxyl group in solution exists as an ion pair so that the O–H bond energy is unaffected by intramolecular changes in the $RCOO^-$ anion, and hence, the ionization is essentially an electrostatic phenomenon. The equation for the calculation of the enthalpy change for proton ionization from electrostatic theory is given in eq 1.[5,6] Though this equation contains parameters which are not easy to assign numerically, it does give an idea of the order of magnitude of ΔH. Solution of this equation by assigning reasonable values to r, D, and $\partial \ln D/\partial T$ gives a small value for the enthalpy change, in agreement with what is observed for carboxyl groups. In contrast, the value of ΔH for proton ionization from the N–H group cannot be explained by electrostatic theory, and the N–H bond must have some covalent character.

$$\Delta H = \frac{-Ze^2}{Dr}\left[1 + \frac{\partial \ln D}{\partial T}\right] \tag{1}$$

The changes in ΔH for proton ionization from the N–H group also cannot be explained by electrostatics and must result from inductive or π interactions between the ring and the substituents.

It is apparent that the $\Delta S°$ values in Table III depend largely on the charge on the anion formed in the reaction and not on the kind of group which is ionizing. This is illustrated by the fact that the entropy changes are about the same for proton ionization from the N–H group in 1,2,3-triazole, benzotriazole, and 4,5-dibromo-1,2,3-triazole. These entropy changes are of the same order of magnitude as those that one would calculate from an electrostatic model.[5,6] This would tend to support the hypothesis that nonelectrostatic considerations are reflected largely in the enthalpy changes and that the entropy change is primarily the result of electrostatic phenomena.

An analysis of the pK data for proton ionization from the N–H group leads one to conclude that the pK

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(6) E. J. King, "Acid-Base Equilibria," Pergamon Press Inc., Oxford, England, 1965, p 156 ff.

values are changed by neutral substituents on the 1,2,3-triazole ring but are not affected by charged carboxyl groups. This point is illustrated if one compares the p*K* values of 4,5-dibromo-1,2,3-triazole and the carboxyl-substituted triazoles with the p*K* value of triazole (Table III). The carboxyl anions on the 4,5-dicarboxylic acid have no effect on the p*K* for the ionization of the N–H proton. In contrast, the p*K* for 4,5-dibromo-1,2,3-triazole is lowered considerably by the bromine substituents in the ring. These facts can be explained by noting that the entropy change for the ionization from the N–H group in the dicarboxylic acid derivative is about three times as great as the entropy change for ionization from 1,2,3-triazole because the proton ionizes in the field of three charges. This fortuitously offsets the decrease in the enthalpy change and the free energy is not affected. In the case of the dibromo derivative, the entropy change is the same as that for triazole and, hence, the decrease in the enthalpy change decreases the free energy change.

Further studies are now being conducted in this laboratory to attempt to determine the mechanism of the very large substituent affect on $\Delta H°$ for proton ionization from the 1,2,3-triazole ring.

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A Study of the Kinetics of the Oxidation of Arsenic(III) by Electrogenerated Iodine in Alkaline Media

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Abstract: The oxidation of As(III) by electrogenerated I_3^- was studied in aqueous media for $8.17 \leq pH \leq 9.17$ using the rotating ring-disk electrode. On the basis of chemical kinetic evidence reported in the literature, it is shown that the mechanism commonly given to account for the observed rate law at low pH is not correct for pH >7. The rate of oxidation of all forms of As(III) is given by $-d[As(III)]/dt = k[I_3^-][H_2AsO_3^-] + k'[I_2][H_2AsO_3^-]$ where $k = (5.65 \pm 0.05) \times 10^6$ l. mol^{-1} sec^{-1} and $k' = (1.75 \pm 0.15) \times 10^8$ l. mol^{-1} sec^{-1}.

The purpose of this research was to investigate the kinetics of the reaction between iodine and As(III) in aqueous solutions of pH >7. Roebuck[2,3] reported the forward rate law for the reaction

$$H_2O + H_3AsO_3 + I_3^- \underset{}{\overset{k_f}{\rightleftharpoons}} H_3AsO_4 + 3I^- + 2H^+ \quad (1)$$

in acidic media to be

$$\frac{-d[As(III)]}{dt} = \frac{k_f[As(III)][I_3^-]}{[I^-]^2[H^+]} = k_{obsd}[As(III)][I_3^-] \quad (2)$$

where $k_f = 1.57 \times 10^{-5}$ mol^2 l.$^{-2}$ sec^{-1}.[4]

The mechanism suggested by Liebhafsky[5] to account for the observed rate law at low pH is

$$\begin{gathered} I_3^- + H_2O \rightleftharpoons HIO + H^+ + 2I^- \\ HIO + H_3AsO_3 \overset{k_f}{\rightleftharpoons} H_3AsO_4 + H^+ + I^- \end{gathered} \quad (3)$$

On the basis of this mechanism[6] and other data,[7,8] it has been suggested that the kinetic behavior of halogens in aqueous media can usually be explained by a mechanism involving the hypohalous acid or anion.

Eigen and Kustin[9] determined the forward rate constant for disproportionation of I_2 using temperature-jump methods. They report $k_f = 3$ sec^{-1} for the reaction

$$I_2 + H_2O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} HIO + H^+ + I^-$$

Combining this result with the dissociation constant for I_3^-, 1.4×10^{-3}, and neglecting k_b, permits one to calculate the maximum rate of production of HIO according to eq 4. However, it is well known that the

$$\frac{d[HIO]}{dt} = \frac{4.2 \times 10^{-3}[I_3^-]}{[I^-]} \quad (4)$$

I_3^-–As(III) reaction is extremely rapid in alkaline media, in conflict with the result predicted by eq 4 for the usual values of the ratio $[I_3^-]/[I^-]$. Thus, the oxidation of As(III) by I_3^- in alkaline media must occur by some mechanism other than that proposed by Liebhafsky for acid media.

A steady-state electrochemical technique, using the rotating ring-disk electrode (rrde), was selected to study this reaction. The rrde has been applied to the study of second-order homogeneous reactions where the reaction is diffusion[10–12] or kinetically[13] controlled.

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