Study of Acidity Constants of 3-, 4-, 5-, and 6-Chloro-*o*-toluidinium Ions in Aqueous Solution and Related Thermodynamic Quantities. I

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The acidity constants of anilinium, simple and 3-, 4-, 5-, and 6-chloro-*o*-toluidinium ions have been studied at seven different temperatures by pH metry in aqueous solution and correlated using the relation $\ln K=A+BT+CT^2$. The values of ΔG, ΔH, ΔS, and ΔC_p have been calculated at different temperatures. The possibility of the additivity in the thermodynamic quantities of these disubstituted anilinium ions has been examined. Hammett type equation has been developed to correlate the acidity constant of these ions at 25°C. Attempt has been made to explain the trends in the thermodynamic quantities of these ions in terms of polar, steric, and solvent effects.

Acidity constants of anilinium, *o*-, *m*-, and *p*-toluidinium and *o*-, *m*-, and *p*-chloroanilinium ions have been reported by Biggs at different temperatures.[1] The heats of ionization of the isomeric xylidinium and toluidinium ions have been determined by Laidler and co-workers by calorimetric method.[2] The present communication deals with the study of the acidity constants of 3-, 4-, 5-, and 6-chloro-*o*-toluidinium ions by pH metry at equally spaced seven temperatures ranging from 15 to 45°C. The acidity constant of each of these ions is correlated with temperature using a three constant equation, $\ln K=A+BT+CT^2$. This equation is used to calculate thermodynamic functions ΔG, ΔH, ΔS, and ΔC_p at all the seven temperatures. The thermodynamic quantities of the ionization of anilinium and *o*-toluidinium ions were required to check the possible additivity in the corresponding thermodynamic quantities of chlorotoluidinium ions. For examining such an additivity, it was desirable to study the acidity constants of these two ions at the corresponding temperatures under the conditions under which the acidity constants of the isomeric chloro-*o*-toluidinium ions were determined. Hence the acidity constants of these two ions were redetermined and the thermodynamic quantities were calculated by the application of the above mentioned equation. Modified Hammett relation is derived and applied to correlate the acidity constants of these *o*-substituted anilinium ions with Hammett σ and ρ constants. Attempt has also been made to interpret the values of the thermodynamic quantities ΔG, ΔH, and ΔS in terms of the polar, steric, and solvent effects.

Experimental

Reagents. Anilinium chlorides were prepared by the following method starting with laboratory grade chemicals. Each aniline derivative was distilled in an all-glass apparatus and the fraction boiling at constant boiling point was collected. The fraction was then redistilled over zinc dust. The liquid thus purified was dissolved in 10 times its weight of dry ether. Dry hydrogen chloride prepared from AR grade chemicals was passed through this solution and the white solid which separated was filtered and washed with ether. The white solid was crystallized from pure ethanol. The crystalline solid was dried over anhydrous calcium chloride in a vacuum desiccator. It was preserved in a dry coloured bottle kept in a vaccum desiccator. The boiling points of the aniline derivatives and the melting points of their anilinium chlorides were in accordance with those reported in literature.[3] The equivalents weights of the anilinium salts agreed within 0.2% of the calculated value.

Apparatus. The pH metric titrations were carried out using Metrohm pH meter E300 with an expanded scale on which pH could be conveniently read up to 0.005 pH units. A Metrohm dosigraph E364 micrometer syringe type burette capable of delivering volume of 0.001 m*l* was used. Metrohm glass electrode EA 100 X and calomel electrode with saturated potassium chloride solution were used. A 100 m*l* pyrex beaker was covered at the top with a special bakelite cork with four wholes, two of which were for the electrodes, one for thermometer and one for admitting the tip of the burette. The solution was stirred magnetically.

Temperature Control. The acidity constants were determined at equally spaced seven different temperatures from 15 to 45°C. The cell temperature was maintained by circulating water from a constant temperature bath into a jacket around the cell. The temperature of the cell was controlled within 0.1°C of the reported value.

Standardization of pH Meter. As pH of the reagent-solutions were found to lie in the range from 3 to 4, 0.05M aqueous solution of potassium hydrogen phthalate and saturated aqueous solution of potassium hydrogen tartarate were considered as suitable buffer solutions for the standardization of the pH meter. The pH values of NBS standard of these buffer solutions at various temperatures were followed while standardizing pH meter at the respective temperatures.[4]

Procedure. A stock solution, 0.01M with respect to the required anilinium chloride and 0.005M with respect to potassium chloride was prepared in distilled water. The three sets of solutions, 0.002, 0.003, and 0.004M, for the actual titration were prepared by diluting 10, 15, and 20 m*l* of the stock solution to 50.0 m*l* by adding ditilled water. The titrations were carried out at these three concentrations at each temperature. Standard potassium hydroxide solution, was prepared using carbonate free potassium hydroxide in triple distilled water. Its strength was adjusted to an exact value around 0.15M. The amount of titrant added each time was so adjusted that pH changes by about 0.05 to 0.10 units for each addition. The titration was carried out almost up to the point of neutrali-

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[1] A. I. Biggs, *J. Chem. Soc.*, **1961**, 2572.

[2] T. W. Zawidzki, H. M. Papee, W. J. Canady, and K. J. Laidler, *Trans. Faraday Soc.*, **55**, 1738 (1959).

[3] I. Heilborn and H. M. Bunbury (Editors in Chief), "Dictionary of Organic Compounds," Eyer and Spottiswoode, London.

[4] R. G. Bates, "Electrometric pH Determinations," John Wiley and Sons, Inc., New York, p. 74.

zation.

As it was not possible to prepare a clear solution of 6-chloro-*o*-toluidinium ion in water, the procedure for titration of this ion was modified. Three solutions which were 0.002, 0.003, and 0.004M with respect to HCl and three other solutions which were 0.002, 0.003, and 0.004 both with respect to HCl and 6-chloro-*o*-toluidinium ion were prepared. They were titrated against the same standard alkali solution.

The pH meter readings for the titration of blank HCl solution and of solution containing both the reagent and HCl of the corresponding strength were plotted against the amount of alkali added on the same graph paper. The readings from the middle portion of graph were selected for calculation.

Results and Discussion

Calculations. At constant ionic strength, the thermodynamic acidity constant $K_a{}^{\mathrm{T}}$ for the reaction

$$\mathrm{BH^+ + H_2O \rightleftharpoons B + H_3O^+} \tag{1}$$

is given by the relation:

$$K_a^{\mathrm{T}} = \frac{[\mathrm{B}](\mathrm{H_3O^+})}{[\mathrm{BH^+}]} \cdot \frac{1}{f_{\mathrm{BH^+}}} = K_a^{\mathrm{M}} \cdot \frac{1}{f_{\mathrm{BH^+}}} \tag{2}$$

$$\therefore \quad \mathrm{p}K_a^{\mathrm{T}} = \mathrm{p}K_a^{\mathrm{M}} + \log f_{\mathrm{BH^+}} \tag{3}$$

where $K_a{}^{\mathrm{M}}$ is called the mixed constant because out of the three terms in the equilibrium expression, [B] and [BH] are concentration terms and (H_3O^+) is an activity term.

Seven to eight titration readings were selected from the middle portion of the titration data in order to evaluate $K_a{}^{\mathrm{T}}$. The activity term (H_3O^+) was calculated from the measured pH of the solution at a given stage in the titration. If [K^+], [B], and [BH^+] are the concentrations of the bracketed terms at the same stage in titration, and if [$BH_0{}^+$] is the original concentration of the solution, it can be proved[5] that

$$[\mathrm{B}] = [\mathrm{K^+}] + [\mathrm{H_3O^+}] \tag{4}$$

$$[\mathrm{BH^+}] = [\mathrm{BH_0{}^+}] - [\mathrm{B}] \tag{5}$$

The concentration of OH^-, which is extremely low in acidic solution, is neglected. The activity coefficient $f_{\mathrm{BH^+}}$ was calculated using the Debye-Hückel limiting law,[6]

$$\log f_i = AZ_i^2\sqrt{I_m} \tag{6}$$

where $A = -1.823 \times 10^6/(DT)^{3/2}$, $Z_i = 1$ and I_m is the ionic strength at the stage of half neutralization. It has been recommended that for titration at low concentrations, the value of the ionic strength at the stage of half neutralization may be used in deriving the DHLL correction.[6] The DHLL corrections were not applied to 6-chloro-*o*-toluidinium ion as the observed scatter in the values of $\mathrm{p}K_a$ of this ion was of the order of the correction to be applied.

The method of calculation of acidity constant for ionization of 6-chloro-*o*-toluidinium chloride was slightly different. The concentration term [B], was obtained by subtracting the hydrogen ion concentration of blank HCl titration at a given stage of titration from the hydrogen ion concentration at the corresponding stage of titration of the solution of the anilinium chloride in HCl of the same strength. [BH^+] is calculated using relation (5).

The values of $\mathrm{p}K_a{}^{\mathrm{T}}$ for anilinium, *o*-toluidinium and 3-, 4-, 5-, and 6-chloro-*o*-toluidinium ions at all the seven temperatures are reported in Table 1. The values of $\mathrm{p}K_a{}^{\mathrm{T}}$ agree within ±0.01 p*K* units except for 6-chloro-*o*-toluidinium ion. For the latter ion the scatter is found to be about ±0.02 p*K* unit.

TABLE 1. p*K* VALUES OF ANILINIUM IONS

	Temperature °C						
	15	20	25	30	35	40	45
Anilinium	4.78	4.70	4.615	4.51	4.425	4.345	4.27
o-Toluidinium	4.58	4.495	4.45	4.345	4.28	4.20	4.12
3-Cl-*o*-T	3.745	3.67	3.62	3.52	3.455	3.385	3.32
4-Cl-*o*-T	3.98	3.92	3.85	3.78	3.705	3.62	3.57
5-Cl-*o*-T	3.55	3.48	3.385	3.34	3.265	3.20	3.15
6-Cl-*o*-T	2.59	—	2.49	2.39	—	2.23	—

Correlation of Acidity Constants and Temperature. Out of the many empirical equations proposed by various workers to correlate acidity constants with temperature,[7–11] the equation

$$\ln K = A + BT + CT^2 \tag{7}$$

is employed to correlate the experimental data reported in the present communication and to evaluate the thermodynamic quantities. This equation was empolyed by Ives and Pyror[10] to correlate successfully the variation of ionization constants of monohalogenoacetic acids with temperature. The selection of the equation is justified by the fact that the equation represents the experimental data within the limits of experimental error. The constants of the equations are evaluated by the application of the method of least squares.

From Eq. (7), the following equations are derived:

$$G = -RAT - RBT^2 - RCT^3 \tag{8}$$

$$H = RBT^2 + 2RCT^3 \tag{9}$$

$$S = 2RBT + 3RCT^2 + RA \tag{10}$$

$$C_p = 2RBT + 6RCT^2 \tag{11}$$

It has been reported that more than one equations may represent the same experimental data almost equally well and that there may be a fair agreement in the values of $\varDelta H$ and $\varDelta S$ calculated by the application of each of the equations. However, the values of $\varDelta C_p$ are found to be different.[12] From this point of view, the values of $\varDelta C_p$ evaulated by the appli-

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[6] A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen and Co., Ltd., London.

[7] a) D. H. Everett and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **35**, 1380 (1939). b) *ibid.*, *Proc. Roy. Soc.* (London), **A169**, 190 (1938).

[8] H. S. Harned and R. A. Robinson, *ibid.*, **36**, 973 (1940).

[9] H. S. Harned and N. D. Embree, *J. Amer. Chem. Soc.*, **56**, 1042, 1050 (1934).

[10] D. J. G. Ives and J. H. Pyror, *J. Chem. Soc.*, **1955**, 2104.

[11] F. S. Feates and D. J. G. Ives, *ibid.*, **1956**, 2798.

[12] David T. Y. Chen and K. J. Laidler, *Trans. Faraday Soc.*, **58**, 480 (1962).

Table 2. Thermodynamic quantities of anilinium ions
Constants of equation $\ln K = A + BT + CT^2$

Ion	Equation	Ion	Equation
Anilinium	$\ln K = -31.5851 + 0.099798T - 0.00009868T^2$	5-Cl-*o*-T	$\ln K = -35.8960 + 0.155257T - 0.00020504T^2$
o-Toluidinium	$\ln K = -13.6471 - 0.0113382T + 0.00007675T^2$	*o*-Chloro-anilinium[a]	$\ln K = -8.1393 - 0.0127182T + 0.00006579T^2$
3-Cl-*o*-T	$\ln K = -20.1652 + 0.04635506T - 0.00002193T^2$	*m*-Chloro-anilinium[a]	$\ln K = -35.4502 + 0.1505216T - 0.0001974T^2$
4-Cl-*o*-T	$\ln K = -15.0409 + 0.0092946T + 0.00003838T^2$	*p*-Chloro-anilinium[a]	$\ln K = -25.8009 + 0.075349T - 0.00006579T^2$

a) p*K* values at five temperatures from Ref. 1.

Temperature T	Anilinium ion	*o*-Toluidinium ion	3-Cl-*o*-T	4-Cl-*o*-T	5-Cl-*o*-T	6-Cl-*o*-T	*o*-Chloro-anilinium ion	*m*-Chloro-anilinium ion	*p*-Chloro-anilinium ion
ΔG kcal·mol^{-1}									
288.16	6.31	6.04	4.94	5.25	4.68	—	—	—	—
293.16	6.29	6.04	4.93	5.25	4.66	—	3.62	4.83	5.45
298.16	6.28	6.04	4.91	5.25	4.64	3.36	3.60	4.81	5.44
303.16	6.26	6.04	4.90	5.24	4.62	—	3.58	4.79	5.42
308.16	6.25	6.03	4.87	5.22	4.60	—	3.56	4.78	5.40
313.16	6.23	6.02	4.85	5.20	4.59	—	3.53	4.77	5.38
318.16	6.21	5.99	4.83	5.18	4.58	—	—	—	—
ΔH kcal·mol^{-1}									
288.16	7.08	5.43	5.56	5.18	6.12	—	—	—	—
293.16	7.16	5.75	5.72	5.43	5.98	—	4.41	5.94	6.28
298.16	7.23	6.08	5.88	5.68	5.82	2.62	4.68	5.79	6.38
303.16	7.30	6.43	6.04	5.94	5.65	—	4.96	5.63	6.47
308.16	7.35	6.78	6.20	6.22	5.45	—	5.25	5.44	6.56
313.16	7.40	7.16	6.36	6.49	5.23	—	5.55	5.24	6.65
318.16	7.44	7.54	6.52	6.78	4.98	—	—	—	—
ΔS cal·deg^{-1}·mol^{-1}									
288.16	2.68	−2.11	2.16	−0.25	4.99	—	—	—	—
293.16	2.95	−1.01	2.70	0.60	4.52	—	2.71	3.79	2.81
298.16	3.20	0.12	3.24	1.47	3.99	2.48	3.62	3.30	3.15
303.16	3.41	1.27	3.76	2.34	3.40	—	4.55	2.76	3.47
308.16	3.59	2.44	4.28	3.22	2.75	—	5.49	2.15	3.77
313.16	3.75	3.64	4.80	4.12	2.04	—	6.46	1.49	4.04
318.16	3.88	4.86	5.31	5.02	1.26	—	—	—	—
ΔC cal·deg^{-1}·mol^{-1}									
298.16	13.7	67.9	31.7	51.7	−33.3	—	54.6	−30.9	19.5

cation of Eq. (8) have been reported at 25°C and no attempt has been made to attach any significance to the calculated value.

The calculated values of thermodynamic quantities for anilinium, *o*-toluidinium, 3-, 4-, and 5-chloro-*o*-toluidinium ions at all temperatures are given in Table 2. The thermodynamic quantities for the ionization of *o*-, *m*-, and *p*-chloroanilinium in aqueous solutions at 25°C were required for examining the possible additivity in the corresponding thermodynamic quantities of isomeric chloro-*o*-toluidinium ions. They were calculated by the application of Eq. (7) to the acidity constants of these ions reported by Biggs[1] at five different temperatures.

The scatter in evaluated acidity constants of 6-chloro-*o*-toluidinium ion was found to be of the order of DHLL correction. Hence it was throught improper to apply this correction to the calculated pK_a. For the same reason it was considered improper to apply Eq. (7) to the data for the purpose of correlating the values of acidity constants with temperature. The values are correlated using the following simplified equation[7b]

$$\log K = A - B/T \qquad (12)$$

The thermodynamic quantities of this ion at 25°C are reported in Table 2.

Additivity of Thermodynamic Quantities. According to Laidler the prediction of thermodynamic quantities for disubstituted anilinium ions from the changes produced when single substituents are introduced sepa-

Table 3. Thermodynamic quantities of $R_1(R_2)C_6H_3NH_3^+ + C_6H_5NH_2 \rightleftharpoons R_1(R_2)C_6H_3NH_2 + C_6H_5NH_3^+$ at 25°C

Acid	pK_a	ΔG kcal·mol^{-1}	ΔH kcal·mol^{-1}	ΔS cal·deg^{-1}·mol^{-1}	ΔG kcal·mol^{-1} (estimated)	ΔH kcal·mol^{-1} (estimated)	ΔS cal·edg^{-1}·mol^{-1} (estimated)
Anilinium	4.615	0.00	0.00	0.00	—	—	—
o-Toluidinium	4.45	−0.24	−1.15	−3.08	—	—	—
o-Chloroanilinium	2.64	−2.68	−2.55	+0.42	—	—	—
m-Chloroanilinium	3.52	−1.47	−1.44	+0.10	—	—	—
p-Chloroanilinium	3.98	−0.84	−0.85	−0.05	—	—	—
3-Cl-*o*-T	3.62	−1.37	−1.35	+0.04	−1.71	−2.59	−2.98
4-Cl-*o*-T	3.85	−1.03	−1.55	−1.73	−1.08	−2.00	−3.13
5-Cl-*o*-T	3.386	−1.64	−1.41	+0.79	−1.71	−2.59	−1.98
6-Cl-*o*-T	2.49	−2.92	−4.61	−5.68	−2.92	−3.70	−2.66

rately in anilinium ion is referred to as additivity.[13] Laidler has analysed the role of polar, steric, and solvent effects in deciding the additivity of thermodynamic quantities. Laidler has also indicated that interpretation of the thermodynamic quantities has proved to be complicated because the above-mentioned effects do not operate independently.[13]

With a view to examining the additivity in the thermodynamic quantities of disubstituted anilinium ions, ionization of anilinium ion in aqueous solution is considered as a reference reaction. The increments in each of the thermodynamic quantities due to introduction of a single substituent is calculated by deducting the value of the particular thermodynamic quantity for the ionization of the mono-substituted anilinium ion (say $RC_6H_4NH_3^+$) from that of the corresponding quantity for the ionization of anilinium ion. The increments in the value of ΔG, ΔH, and ΔS thus calculated may be considered to be the corresponding thermodynamic quantities of the following reaction

$$ArNH_3^+ + PhNH_2 \rightleftharpoons ArNH_2 + PhNH_3^+ \qquad (13)$$

These values are shown in Table 3.

The increments in a particular thermodynamic quantity due to introduction of each of the substituents separately in the required position in anilinium ion are added up to calculate the increments due to the introduction of the two substituents in their respective positions in disubstituted anilinium ion.

Examination of the values shown in Table 3 indicates that additivity is observed in ΔG values of 4-, 5-, and 6-chloro-*o*-toluidinium ions. It is not observed in ΔG value of 3-chloro-*o*-toluidinium ion.

The additivity is not observed in ΔH and ΔS values of 3-, 4-, 5-, and 6-chloro-*o*-toluidinium ions. The predicted and the experimental values differ appreciably. However, the fact that the additivity is observed in ΔG values for the ionization of 4-, 5-, and 6-chloro-*o*-toluidinium ions, suggests that through the variations in ΔH and ΔS appear to be quite random, their variations have occurred in a compensating manner as suggested by Laidler.[13]

Linear Free Energy Relationships. The acidity constants of *m*- and *p*-substituted anilinium ions are correlated by the application of Hammett type equation.[14] The value of the reaction constant for the ionization of anilinium ions in aqueous solution at 25°C is reported by Jåffe to be 2.767.[15] The substituent constants for ortho substituents are not obtainable mainly because of the variable nature of steric and conjugation effects of such group in different reactions. According to Clark and Perrin,[14] apparent σ-ortho constants which are valid only for the given reaction conditions under which they are determined can be used satisfactorily in conjunction with the normal σ-meta and σ-para constants for prediction. The method suggested by Clark and Perrin[14] is used in arriving at the following equation on the basis of the values of acidity constants reported in Table 4 for *o*-substituted anilinium ions at 25°C.

$$pK_a = 4.615 - 2.85\sum\sigma \qquad (14)$$

Table 4. Linear free energy relations in *o*-toluidinium ions at 25°C. In aqueous solution
$pK_a = 4.615 - 2.85\sum\sigma$

Acid	pK_a Reported at 25°C	$\sum\sigma$	pK_a Estimated
o-Toluidinium	4.45	+0.06[a]	4.44
2:3-Xylidinium	4.70[16]	−0.01	4.64
2:4-Xylidinium	4.89[16]	−0.11	4.93
2:5-Xylidinium	4.53[16]	−0.01	4.645
2:6-Xylidinium	3.95[16]	+0.12	4.27
o-Chloroanilinium	2.64[1]	+0.71[b]	2.59
3-Cl-*o*-T	3.62	+0.43	3.39
4-Cl-*o*-T	3.85	+0.29	3.785
5-Cl-*o*-T	3.386	+0.43	3.39
6-Cl-*o*-T	2.49	+0.77	2.42

a) *o*-Me = +0.06, *m*-Me = −0.07,[14] *p*-Me = −0.17[14]
b) *o*-Cl = +0.71, *m*-Cl = +0.37,[14] *p*-Cl = +0.23[14]

The apparent σ-ortho constants for methyl and chlorine are calculated for ionization of *o*-substituted anilinium ions in aqueous solution at 25°C. The normal Hammett equation was used for this purpose.

$$\log (K/K_0) = \rho \cdot \sigma \qquad (15)$$

The value of ρ was taken to be equal to 2.767.[15]

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[13] K. J. Laidler, *Trans. Faraday Soc.*, **55**, 1725 (1959).

[14] J. Clark and D. D. Perrin, *Quart. Rev.*, **28**, (3) 295 (1954).

[15] H. H. Jåffe, *Chem. Rev.*, **53**, 191 (1953).

[16] R. N. Beale, *J. Chem. Soc.*, **1954**, 4494.

The value of pK for anilinium ion was taken to be 4.615 (pK_o) at 25°C. The reported σ-meta and σ-para constants of methyl and chlorine groups were used.

A comparison of the experimental and estimated pK values indicates that except for 2:6-xylidinium and 3-chloro-*o*-toluidinium ion, there is a good agreement. As reported in the preceding section additivity is not observed in ΔG values of 3-chloro-*o*-toluidinium ions.

Interpretation of the Results

The fact that *o*-toluidinium ion is a stronger acid than anilinium ion is contrary to expectation on the basis of the inductive effect of methyl group ortho to NH_3^+ group. As compared to the ionization of anilinium ion, the ionization of *o*-toluidinium ion is less endothermic and less random. The contribution of the entropy effect to the ΔG values of *o*-toluidinium is very small. ($T\Delta S=0.036$ kcal·mol^{-1})

Molecular model for *o*-toluidinium ion constructed using Catalin Molecular Models showed that the CH_3 and NH_3^+ groups could be just accommodated in the ortho positions only in certain conformations. In such a situation, the interaction between the two groups through the π-electron system of benzene may not be completely restricted. However, the space around NH_3^+ is partly occupied in its immediate vicinity by the ortho methyl groups. Therefore, the extent of solvation will be reduced proportionately. The interaction between the electron releasing methyl group and the positive charge on the nitrogen atom of NH_3^+, will disperse this positive charge on the nitrogen atom. This will reduce the extent of solvation of the *o*-toluidinium ion and make the *o*-toluidinium ion more random. Hence, the process of ionization of *o*-toluidinium ion will proceed with a smaller entropy change. This explains why ΔS is smaller for ionization of this ion than that of anilinium ion.

The fact that ionization of *o*-toluidinium ion is less endothermic than that of anilinium ion suggests that the steric and solvent effects play a more important role than the polar effect. Such a view is also expressed by Brown and co-workers.[17]

The isomeric chloroanilinium ions are stronger acids than anilinium ion. This seems to be due to the presence of electron attracting chlorine atom which makes the release of protons easier. The entropy changes for the ionization of all the three chloroanilinium ions are very nearly the same as they do not differ much from that of the ionization of anilinium ion. Therefore the extent of solvation and hence stability induced by solvation will most probably be the same for all these ions. Hence the difference in ΔH values may possibly be due to the difference in the polar effects operating in bare chloroanilinium ions.

The trends in the thermodynamic quantities of the isomeric 3-, 4-, 5-, and 6-chloro-*o*-toluidinium ions are not explicable simply from the knowledge of the manner in which a particular property is affected by the introduction of a single substituent, methyl or chlorine, in the required position in anilinium ion. It is difficult and perhaps impossible to predict the nature of the possible interactions between the methyl and chlorine substituents in a chlorine substituted *o*-toluidinium ions.

It is also not reasonable to assume that each one of these groups will influence the reaction site independently. Hence no attempt is made to explain the trends in the thermodynamic quantities of these ions. The question of 3-chloro- and 6-chloro-*o*-toluidinium ions is considered because of their peculiar structures.

The molecular model for 3-chloro-*o*-toluidinium ion shows that it is possible to accommodate the three groups respectively in three consecutive positions on the benzene nucleus if NH_3^+ and CH_3 groups take up certain conformations. The methyl and chlorine substituents which are placed in ortho position with respect to each other have opposite polarities. It is quite possible that the methyl group may be pushed nearer to the chlorine atom and away from the NH_3^+ group. Due to this it will make the space around the NH_3^+ group roomier and its interaction with NH_3^+ group weaker. This may explain why ionization of 3-chloro-*o*-toluidinium ion is more random than that of *o*-toluidinium ion.

6-Chloro-*o*-toluidinium ion is the strongest acid of all the four isomeric chloro-*o*-toluidinium ions. The steric and solvent effects are likely to play a prominent role in the ionization of this ion. The space around the NH_3^+ group in this ion is occupied by the methyl and chlorine substituents placed in ortho position to NH_3^+ group. This will reduce the number of water molecules that can associate with NH_3^+ group and will increase the randomness of the ion. It is likely that under the given situation its randomness exceedes that of the hydronium ion. The ionization of 6-chloro-*o*-toluidinium ion may then proceed with decrease in randomness as has been observed. The decreased solvation of this ion will increase its enthalpy. Therefore, the ionization of this ion will be less endothermic than that of *o*-toluidinium or anilinium ion.

The authors thank Professor Dr. R. D. Patel and Dr. C. K. Patel for taking keen interest in the work and making helpful suggestions.

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[17] H. C. Brown and A. Cahn, *J. Amer. Chem. Soc.*, **72**, 2939 (1950).