Thermochemistry of the 2,2′-Bipyridylinium Ion in Aquo–Organic Media at 25 °C

Amit Kumar Ray
Department of Chemistry, Serampore College, Hooghly, West Bengal, India

A method of determining the heat of reaction from calorimetric data alone has been applied to the investigation of the reaction of 2,2′-bipyridyl (bpy) with hydrogen ion in 10, 20, 30, and 45% methanol–water, ethanol–water, and dioxane–water at 25 °C. The data are taken assuming the existence of one species of formula (bpy)H$^+$ according to Kolthoff. The values of $\Delta H°$ in kilocalories per mole are reported in Table I.

Heat of formation of 2,2′-bipyridylinium ion in mixed solvent is measured directly by a new type of calorimeter. Data are treated by assuming the existence of one species, as Kolthoff et al. (*5*) established that the species present in a solution of a small concentration of 2,2′-bipyridyl in the presence of a large H$^+$ ion concentration is a 1:1 complex. In the present communication, $\Delta H°$ for the formation of (bpy)H$^+$ in different mixed meda is reported.

Apparatus

The calorimeter consists of a Dewar flask with a stopper of insulation material (styrofoam) through which electrical leads and a stirrer pass. The temperature monitoring system consists of thermistors (VECO'S glass probe) wired as two opposite arms of a Wheatstone bridge. One of its arms contains three thermistors (VECO'S glass probe 2 K at 25 °C) in parallel and the opposite arm contains one thermistor (1 K at 25 °C). The remaining two arms consist of standard resistances submerged in an oil bath. The balancing component (variable unit) on the circuit is the parallel adjustable resistance attached to one of the standard resistance arms. The completed unit is placed wholly in a thermostat at 25 °C controlled within ±0.05 °C. A spot galvanometer is used as null detector. The heater is made of platinum wire and its circuit is similar to that of O'Hara et al. (*6*). A propeller operated at 100 rpm by a precision motor is used to stir the calorimeter liquid. The measuring strength of the current is taken at 0.002 A, and the sensitivity of the bridge is in the order of 1×10^{-5} °C per ten units resistance change. The electrical calibration is checked periodically by chemical calibration. Chemical reactions used to check the electrical calibration are the neutralization reaction of $HClO_4$ by NaOH and the determination of pK and ΔH values of HSO_4^- and HPO_4^{2-} by the entropy titration technique (*3*). A chart of the temperatures of the medium with the corresponding values of resistances in the variable arm is prepared from electrical calibration.

Experimental Section

The 2,2′-bipyridyl solution is prepared by direct weighing and dissolving 2,2′-bipyridyl (G. R. E. Merck) in the required medium. Perchloric acid is Merck's reagent grade. Any dilution for the experiment is made with conductivity water. The bipyridyl solution of ~250 ml is taken in a reaction vessel and titrant acid solution of ~5–10 ml is taken in a thin-walled glass bulb immersed in the solution which is maintained at 25 °C by the calibration heater. All solutions are left for 4–5 h to attain equilibrium with the reaction vessel. The variable arm of the bridge is adjusted so that the galvanometer gives no deflection. If the galvanometer remains steady for about 5 min, the system is considered to be at equilibrium and optimum for the experimental run. The system studied in the present work is such that the reaction is fast and the heat liberated is instantaneous. At equilibrium, the bulb is broken mechanically and the heat change is measured. Temperatures of the medium against the times which covered the periods of reactions as well as before and after the reactions are then plotted. The curve obtained is divided into three parts. The first part is nearly a straight line which covers the period before the addition of the reacting species, the middle part where the change of temperature is very sharp covers the period of reaction, and the last part is nearly a straight line which covers the period after the reaction is over. Now two tangents are drawn on the first and the third part of the curve. The perpendicular distance between the two tangents passes through the center of the second part of the curve and is the correct temperature change. A blank run is made for every reaction in each of the different media and the net change of heat (including the heat change due to bulb breakage) is less than 1 cal in every case.

Table I. Heat of Formation of 2,2′-Bipyridylinium in Aquo–Organic Media at 25 °C

Wt % of organic solvent in water (X)	Organic solvent Ethanol	 Methanol	 Dioxane
10	3.956 ± 0.007	3.903 ± 0.009	4.015 ± 0.016
20	4.391 ± 0.012	4.114 ± 0.027	4.435 ± 0.027
30	4.173 ± 0.025	3.756 ± 0.053	4.135 ± 0.060
45	3.322 ± 0.022	3.281 ± 0.058	3.507 ± 0.096

Results

According to Kolthoff et al. (*5*), bipyridyl in pH less than 3 is present as (bpy)H$^+$. Therefore, the net heat change due to the reaction will be $Q = \Delta Hn$, where ΔH is the heat of reaction and n is the number of moles of (bpy)H$^+$ ions which are equal to the moles of bipyridyl in the solution. The present work is done in solutions having low ionic strength (at pH just less than 3) because it is reasonable to assume that the activity coefficient ratio tends to unity and the ΔH values are the thermodynamic $\Delta H°$ values. The change in heat is a function of the number of moles of bipyridyl forming (bpy)H$^+$ and corresponding ΔH values are reported in Table I.

Discussion

In the present work, the $\Delta H°$ values for the formation of (bpy)H$^+$ ion 10, 20, 30, and 45% ethanol-water, methanol–water, and dioxane–water media have been estimated. On extrapolation of organic solvent to zero percentage, the $\Delta H°$ value for aqueous medium is found to be equal to 3.60 kcal mol^{-1}. This value agrees with the calorimetric value of 3.65 kcal mol^{-1} given by Anderegg (*2*) where the investigation was made in a medium of moderately high ionic strength. The value of 2 kcal mol^{-1} for $\Delta H°$ in aqueous medium given by Irving et al. (*4*) is too low, though his measurements were made potentiometrically. It can be seen from the values of ΔH° in different percentages of organic media that the ΔH° value in a medium with lower percentage of organic component is within experimental error and linear in composition and that such a value with higher percentage of organic component passes through a maximum. According to Arnett et al. (*1*), the addition of polar solvent (ethanol, methanol) up to a mole fraction of 0.1 increases the structure in the solution and at that composition the maximum order is obtained. Any addition in polar solvent can no longer build structure without interfering with the established order in the system. Thus many properties of the mixture such as molar volume, activity coefficient, sound velocity, and temperature at maximum density of water show maximum at this composition.

Literature Cited

(1) Arnett, E. M., Bentrude, W. C., Burke, J. J., Dugglby, P., *J. Am. Chem. Soc.*, **87**, 1541 (1965).
(2) Anderegg, H., *Helv. Chim. Acta*, **46**, 1813 (1963).
(3) Christensen, J. J., Izatt, R. M., Hansen, L. D., Partridge, J. A., *J. Phys. Chem.*, **70**, 2003 (1966).
(4) Irving, H., Mellor, D. H., *J. Chem. Soc.*, 5222 (1962).
(5) Lee, T. S., Kolthoff, I. M., Leussing, D. S., *J. Am. Chem. Soc.*, **70**, 2348 (1948).
(6) O'Hara, W. F., Wu, C.-H., Hepler, L. G., *J. Chem. Educ.*, **38**, 512 (1961).

Received for review June 26, 1975. Accepted August 30, 1976.

PVT Surface and Thermodynamic Properties of *n*-Pentane

Tarun R. Das and Charles O. Reed, Jr.†
Department of Chemistry, Thermodynamics Research Center, Texas A&M University, College Station, Texas 77843

Philip T. Eubank*
Department of Chemical Engineering and Thermodynamics Research Center, Texas A&M University, College Station, Texas 77843

Selected values of vapor pressure, specific volume, enthalpy, and entropy are presented for the saturated liquid and vapor states of *n*-pentane from normal boiling point (309.19 K) to the critical point (469.65 K). Experimental values of the density, together with the saturated vapor densities, were fitted to a differential regional Benedict–Webb–Rubin (DR-BWR) equation of state; compressibility factors were generated from 309 to 600 K with pressure to 700 atm. Thermodynamic properties of the real gas, $H - H^0$, $(H - H^0)/T$, $A - A^0$, $S - S^0$, $S - S^\mathrm{i}$, $G - G^0$, $(G - G^0)/T$, $G - G^\mathrm{i}$, and f/P, were also calculated from the classical relationships.

A previous correlation study (*5*) presents both vapor–liquid coexistence and superheated vapor thermodynamic properties of *n*-pentane. The present compilation is part of a general revision of the j-tables of the API Research Project 44 (*26*) for C_1–C_5 alkanes.

Physical Constants

Table I is a list of the physical constants and conversion factors (*29*) used in this investigation. A summary of selected, experimentally determined, critical constants is shown in Table II. The present set of critical constants ($T_c = 469.65 \pm 0.15$ K; $P_c = 33.25 \pm 0.10$ atm; $\rho_c = 0.237 \pm 0.005$ g cm^{-3}) is based on the modern measurements of Beattie et al. (*2*), Jordan and Kay (*13*), Partington et al. (*20*), and Ambrose et al. (*1*). These critical constants are the same as those selected by Kudchadker et al. (*15*) and differ but slightly from those selected earlier by Kobe and Lynn (*14*).

Vapor Pressure

A Frost–Kalkwarf vapor-pressure equation was used with the parameters determined to fit the experimental literature values from the normal boiling point (NBP) to the CP.

$$\log P = 17.306\,98 - 1971.73/T - 4.393\,06 \log T + 997.021(P/T^2) \quad (1)$$

where P is in atm and T is in K.

This equation correlates the measurements of Beattie et al. (*2*), Li and Canjar (*16*), Sage and Lacey (*24*), Sage et al. (*25*), and Willingham et al. (*31*) with an average deivation of 0.037 atm. In addition, the equation is in approximate agreement (average deviation of 0.06 atm) with data of Messerly and Kennedy (*18*), Nicolini (*19*), and Tickner and Lossing (*28*), which were not used to determine the constants of eq 1.

At the NBP of 309.19 K and the CP of 469.65 K, the equation agrees exactly with the experimental values. The equation is believed to be accurate to ±0.29% from 300 K to CP, with a maximum uncertainty of ±0.1 atm near the CP. Table III, the selected saturation properties, contains the calculated vapor pressure and its temperature derivative from the NBP to the CP.

Saturated Liquid Volume

The available measurements are those of Calengaert (*4*) (288 K), Carney (*6*) (243–293 K), Dornte and Smyth (*8*) (263–303 K), Li and Canjar (*16*) (423–448 K), Sage and Lacey (*24*) (311–444 K), Sage et al. (*25*) (294–378 K), NGAA (*27*) (228–334 K); Wibout et al. (*30*) (288–293 K), and Young (*32*) (273–466 K).

Selected data from the above references were fitted to a modified Guggenheim equation (*12*) which was further modified as shown below to pass through the CP. The constants of the equation were evaluated for two temperature zones meeting at 323.15 K.

$$\rho_\mathrm{SL} = (\rho_\mathrm{L} + A\theta + B\theta^2)(1.0 + 1.0\theta + 0.25\theta^3) \quad (2)$$

where $\theta = (1 - T/T_\mathrm{L})^{1/3}$, T (K), and ρ (g cm^{-3}). Constants of eq

---

† Deceased.