formation by a reaction of type 9 to compete effectively with the process of diffusion to radicals.

Effect of Freezing on Organic Yields.—When neutron irradiation is carried out in the solid phase at liquid air temperatures the hot atoms are confronted by a more dense and more rigid wall of molecules than in the liquid. Their chance of penetrating this wall without breaking chemical bonds may be much less and hence the density of radical formation may be expected to be greater than in the liquid and the probability that the tagged atom will react with a radical rather than undergo competing reactions with other molecules of the medium is increased. This fact may account for the much higher organic yield in solid ethyl bromide and chloride at liquid air temperatures than in the corresponding liquids. Increased caging effects in the solid may also contribute to the increase in yield.

Effect of Dilution of Alkyl Chlorides with Hexane.—A part of the observed increase in organic yield when ethyl bromide or iodide is diluted with hexane may be due to the decreased likelihood of inorganic radicals (Br or I) being available for combination with the tagged atom and part to the increased density of organic radical formation in a medium made up of the relatively large intertwined hexane molecules.

Effect of Chain Length of Hydrocarbon Solvent.—Among the possible explanations of the observation that the organic yield of iodine in hydrocarbons increases with increasing chain length of the hydrocarbon are: (1) the fact that the ratio of C–C bonds to C–H bonds goes up with increase in chain length; (2) the caging efficiency of the medium may go up with chain length because of the increasing mass, size and possibility of intertwining of the molecules, and the density of radical production by the hot atom may increase similarly. The fact that the organic yield in the series of hydrocarbons is less when the hot atoms originate from I_2 than when they originate from ethyl iodide is probably due to the scavenging effect of the elemental iodine on radicals.

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[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Heat of Neutralization Studies at High Acid–Base Concentrations. I. Sodium Hydroxide–Hydrochloric Acid[1]

BY PAUL BENDER AND WENDELL J. BIERMANN[2]

The heats of neutralization of sodium hydroxide and hydrochloric acid solutions have been measured at 25° for concentrations from 3 to 16 molal, with an accuracy of 0.1% or better. The results have been employed to show the consistency of the existing thermochemical data for the various solute species involved, and lead to the proposal of the value of −13,320 calories per mole for the heat of neutralization at infinite dilution at 25°.

Aside from their intrinsic interest, heat of neutralization measurements may be used to check the consistency of the existing thermochemical data for the various solute species involved. A program of such measurements at high acid–base concentrations has been initiated in this Laboratory to extend the range of previous work in this field; the system sodium hydroxide–hydrochloric acid has been studied first because of the extensive thermochemical data available for comparison.

Experimental Details

Calorimeter.—The isothermal jacket calorimeter was essentially of the design recommended by Dickinson[3] for bomb calorimetry. A mercury thermoregulator was used to control the jacket temperature. The graphical method of Dickinson was employed for the calculation of the corrected temperature rise in the calorimeter.[3]

A tubular electric heating coil (*v.i.*) was suspended rigidly from the calorimeter can cover, concentric with the stirrer shaft; a small propeller blade located inside the heater shell insured a good circulation of water through it. The stirrer was driven by a synchronous motor at 400 r.p.m., a rate shown by test to provide adequate stirring with the reaction vessel stationary.

Reaction Vessel.—The gold-lined, cylindrical stainless-steel reaction vessel was of two piece construction. Closure was effected on a Teflon gasket, an extension of which within the bomb held in place a cylindrical platinum container, of 175-cc. capacity, for the hydrochloric acid solution. This container was initially covered by a sandwich of two pieces of 0.0003″ gold foil sealed together and to the cup flange by a thin film of silicone stopcock grease. In this way a diaphragm readily broken yet free from pinholes was obtained. The quantity of stopcock grease employed was standardized. A Teflon striker, with a gold wire point, pivoted on a gold wire support fastened to the Teflon gasket, was provided to insure rupture of the gold foil seal the first time the bomb turned over.

The stand made to hold the reaction vessel in the calorimeter can was constructed to permit end-over-end rotation of the vessel. This rotation produced rapid and complete mixing of the reacting solutions, which otherwise would have been greatly complicated by the violence with which the reaction takes place. A geared-head synchronous motor gave a rotation frequency of 10 r.p.m. The two drive shafts entering the calorimeter can had Lucite inserts to minimize heat transfer.

Temperature Measurements.—All temperature measurements were made with a type 8160 "calorimetric" platinum resistance thermometer constructed and calibrated by the Leeds and Northrup Company and checked by comparison with their type 8163 "research" platinum thermometers certified by the National Bureau of Standards. The Mueller bridge, made by the Rubicon Company, was thermostatted, and was calibrated in terms of a standard resistor certified by the National Bureau of Standards and supplied by the Electrical Standards Laboratory of the University of Wisconsin through the courtesy of Professor L. C. Larsen.

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(1) Presented at the Cleveland Meeting of the American Chemical Society, April, 1951.

(2) Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, Canada.

(3) H. C. Dickinson, Bur. Standards Scientific Paper No. 230 (1914).

The sensitivity of the galvanometer was 0.0002° per millimeter deflection at the scale distance of two meters.

An electric stop-watch was used for time measurements, and the required time–temperature data were recorded photographically. The conventional method of recording the time at which a preselected temperature was reached was employed. When the bridge came into balance, a microswitch was closed momentarily, actuating an electrically driven Air Force GSAP camera focused (by addition of a +1-diopter portrait attachment to its fixed focus lens system) on the bridge and timer. While the running current of the 28 v. d. c. camera motor is only 1 ampere, the starting surge is of the order of 15 to 20 amperes. To supply this demand conveniently the 800-cycle generator and other extraneous parts of a 28-volt, 40-ampere input surplus inverter were removed, and the inverter motor driven by an a.c. motor as a self-excited generator. Operated at a speed about 20% above its normal rating, this unit supplied the required power for the camera.

The starting time of the camera was approximately $^1/_{32}$ second, and approximately 8 frames had to be exposed in recording a point. At a film speed of 32 frames per second a single R-2 Reflectorflood bulb gave adequate illumination from a distance of one meter. Eastman Cine-Kodak Super X or equivalent 16-mm. film was employed; development was done in large beakers using Ansco M-H Title Developer. Films were read with the help of a simple film-editing viewer.

Calibration.—The heat capacity of the system was determined electrically in the standard fashion; the data of Osborne, Stimson and Ginnings[4] for the specific heat of water were used. In the calibration runs the bomb was set up as for a neutralization run except that it was loaded with distilled water. After preliminary test runs, five heat capacity determinations were made and the results averaged to give the value employed in later calculations; a precision of 0.03% was obtained in these measurements.

The use of a comparatively high resistance (*ca.* 100 ohm) heating coil together with a stable electronically regulated d.c. power supply was prompted by experience with such a combination in flow calorimetric research now in progress here. The heating period was timed with a precision electric timer, made by the Standard Electric Time Company, actuated by a high speed DPDT relay which also served to switch the power supply from a dummy load matched to the heater coil.

The heater was constructed as recommended by Murphy[5] from 26 gage Advance wire wound on a threaded and anodized cylindrical aluminum form which was then completely encased in a metal shell. This heater showed excellent thermal lag characteristics and could withstand a power dissipation as high as 250 watts. The power supply was of conventional design; the variable output voltage contained less than 1 part in 500,000 ripple at maximum current (*ca.* 1.5 amperes), and the regulation was excellent. Over the ten-minute heating periods employed fluctuations were negligible; a slow drift of the output voltage amounting to a maximum of 0.005 to 0.01% was encountered. The electronic supply thus was at least as good as the conventional storage battery source.

To substantiate the calibration procedure a comparison was made of the heat capacity of the system with a double valve oxygen bomb replacing the neutralization reaction vessel assembly, as determined by the electrical method and by use of Bureau of Standards benzoic acid as a combustion standard. The two results agreed within the previously specified precision of our electrical calibration.

Solutions.—The hydrochloric acid solutions were prepared from reagent grade concentrated hydrochloric acid and analyzed by the gravimetric silver chloride method.

All sodium hydroxide solutions were prepared by dilution of a saturated stock solution to minimize contamination with sodium carbonate, and were stored in bottles lined with ceresine wax. In an indirect analysis a weighed sample of solution was evaporated to dryness with an excess of hydrochloric acid, the sodium chloride residue baked to eliminate the excess hydrogen chloride, and a gravimetric chloride determination made by means of silver chloride.

The accuracy of the chloride determinations is estimated at 0.03%, except for the more concentrated acid solutions where less satisfactory results were obtained due to the volatilization of hydrogen chloride during the sampling process. The latter difficulty was of minor consequence, however, since a slight excess of acid was always used, the neutralization process being defined quantitatively by the weight of sodium hydroxide solution employed. All dilutions required in the preparation of the solutions were made quantitatively to permit an internal check on the consistency of the analyses.

Calibrated weights were used in all work described in this paper, and all weights reported have been corrected to vacuum.

Calculations and Results

The heat capacity of the products of the reaction was used in the calculation of the total heat capacity of the calorimetric system; the measured heat of reaction therefore referred to the initial temperature. The values used for the specific heats of sodium chloride solutions were based on a critical comparison of the results of Bousfield and Bousfield,[6] Bogorodskii and Dezideriev[7] and Randall and Rossini.[8] The required data on the heat of crystallization of sodium chloride and the solubility of sodium chloride as a function of temperature were taken from the results of Wüst and Lange,[9] and Berkeley,[10] respectively. As previously noted the final solution contained a small amount of hydrochloric acid; its contribution to the heat capacity of the solution was considered to be the same as that of the sodium chloride present.

The final result desired was the heat of reaction at 25° corresponding at low concentrations ($m' \leq m_s$), to the reaction

$$\left[\mathrm{NaOH} + \frac{55.51}{m}\,\mathrm{H_2O}\right] + \left[\mathrm{HCl} + \frac{55.51}{m}\,\mathrm{H_2O}\right] \longrightarrow \left[\mathrm{NaCl} + \frac{55.51}{m'}\,\mathrm{H_2O}\right] \quad \text{(I)}$$

and at high concentrations, ($m' \geq m_s$), to the reaction

$$\left[\mathrm{NaOH} + \frac{55.51}{m}\,\mathrm{H_2O}\right] + \left[\mathrm{HCl} + \frac{55.51}{m}\,\mathrm{H_2O}\right] \longrightarrow \left[\frac{m_s}{m'}\,\mathrm{NaCl} + \frac{55.51}{m'}\,\mathrm{H_2O}\right] + \left(1 - \frac{m_s}{m'}\right)\mathrm{NaCl_{(s)}} \quad \text{(II)}$$

where

$$m' = \frac{55.51m}{111.02 + m}$$

m_s = molality saturated aqueous NaCl solution at 25°

Conventional methods were employed in correcting the measured heat of the bomb reaction for the following deviations from the conditions specified above:

(a) at high acid concentrations the vapor phase in the platinum cup contained an appreciable amount of hydrogen chloride. (b) A net transfer of water between the vapor and solution phases in the bomb took place because of the differing vapor pressures of the several solutions. (c) The temperature for which the measured heat of reaction was obtained was not exactly 25°. (d) A slight excess of hydrochloric acid was used. (e) The initial molalities of the sodium hydroxide and hydrochloric acid solutions were not exactly equal.

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(5) G. W. Murphy, *Rev. Sci. Instruments*, **20**, 372 (1949).

(6) W. W. Bousfield and W. M. Bousfield, *Trans. Roy. Soc. London*, **218A**, 119 (1919).

(7) A. Ya. Bogorodskii and G. P. Dezideriev, *Kazanskii Khimiko-tekhnologicheski instituta Trudy*, **4–5**, 29 (1935).

(8) M. Randall and F. D. Rossini, This Journal, **51**, 323 (1929).

(9) J. Wüst and E. Lange, *Z. physik. Chem.*, **116**, 161 (1925).

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For the hydrochloric acid solutions the results of Sturtevant[11] and Akerlof and Teare[12] for the relative enthalpies were used. The values of $\overline{L}_1$ tabulated in the paper of Akerlof and Teare were found to be in arithmetic error, and were replaced by values calculated directly from their equations. Specific heat data for hydrochloric acid solutions have been given by Vrevski and Kaigorodov[13]; their results were found to be in good agreement with comparison values calculated from the relative partial molal heat capacities given by Akerlof and Teare[12] in combination with the values of Rossini[14] for $\overline{C}^{\circ}_{\mathrm{P}_2}$ and those of Osborne, Stimson and Ginnings[4] for $\overline{C}^{\circ}_{\mathrm{P}_1}$. For the most dilute solutions Sturtevant[15] has given values for the relative enthalpies of sodium hydroxide solutions at 25°; for higher concentrations the relative enthalpies at 25° were calculated from those given at 20° by Bertetti and McCabe,[16] together with the specific heat data of Bertetti and McCabe and the values of Gucker and Schminke,[17] and Osborne, Stimson and Ginnings[4] for $\overline{C}^{\circ}_{\mathrm{P}_2}$ and $\overline{C}^{\circ}_{\mathrm{P}_1}$, respectively. The results given by Bertetti and McCabe were recalculated on the basis of the data of Sturtevant for the dilute range, since their reported values were based on heat of dilution measurements at high concentrations combined with the results of Richards and Gucker[18] at low concentrations. All vapor pressure data were obtained from the International Critical Tables, as was the enthalpy of hydrogen chloride gas relative to the infinitely dilute aqueous solution. The common molality m to which the observed heat of reaction was corrected was in each case that giving a value of m' equal to the molality of the sodium chloride solution produced experimentally.

The experimental results are summarized in Table I; these values are believed accurate to 0.1% or better. The data are therefore not sufficiently accurate to show the discontinuity at the concentration (m = 13.85) above which solid sodium chloride is precipitated in the reaction, since it may readily be shown that the discontinuity in slope at this point amounts to only 14 calories per mole because of the low heat of crystallization of sodium chloride.

Discussion

The only reliable heat of neutralization data previously available at concentrations approximating those of this work are those of Richards and Rowe[19] at 2.220 molal, reported in 20° calories at 20°. Their result, corrected to 25°, and expressed in defined calories, becomes −14,040 cal./mole; extrapolation of the present data gives the comparison value of −14,030 cal./mole, in excellent agreement and confirming the confidence regularly placed in the work of Richards.

The heat of neutralization as a function of composition is fixed by the relations

$m' \leqslant m_s$

$$\Delta H_{\mathrm{N}} = \Delta H^{\circ}_{\mathrm{N}} + \overline{L}_{2(\mathrm{NaCl},\, m')} - \overline{L}_{2(\mathrm{NaOH},\, m)} - \overline{L}_{2(\mathrm{HCl},\, m)} + \frac{55.51}{m}\left[\frac{m}{m'}\,\overline{L}_{1(\mathrm{NaCl},\, m')} - \overline{L}_{1(\mathrm{NaOH},\, m)} - \overline{L}_{\mathrm{H1(Cl},\, m)}\right]$$

$m' \geqslant m_s$

$$\Delta H_{\mathrm{N}} = \Delta H^{\circ}_{\mathrm{N}} + \overline{L}_{2(\mathrm{NaCl},\, m_s)} - \overline{L}_{2(\mathrm{NaOH},\, m)} - \overline{L}_{2(\mathrm{HCl},\, m)} + \left(1 - \frac{m_s}{m'}\right)\left[H_{(\mathrm{NaCl},\, s)} - \overline{H}_{2(\mathrm{NaCl},\, m_s)}\right] + \frac{55.51}{m}\left[\frac{m}{m'}\,\overline{L}_{1(\mathrm{NaCl},\, m_s)} - \overline{L}_{1(\mathrm{NaOH},\, m)} - \overline{L}_{1(\mathrm{HCl},\, m)}\right]$$

For direct use of these equations there is required the standard heat of neutralization, which must be evaluated indirectly because the heat of neutralization measurements so far reported do not extend to sufficiently low concentrations to justify direct extrapolation to infinite dilution. As a reference point for this indirect calculation the heat of neutralization at 3.239 molal was determined in quadruplicate, with an average deviation of six calories from the mean of the four results; the experimental conditions were adjusted to make negligible the corrections previously referred to. This value was combined with the relative enthalpy data of Sturtevant for hydrochloric acid and sodium hydroxide solutions and of Robinson[20] for sodium chloride solutions to give for $\Delta H^{\circ}_{\mathrm{N}}$ the value of −13,320 defined calories per mole. The corresponding value derived from the experimental heat of neutralization at 3.014 molal was −13,321 calories, in precise agreement. The uncertainty in this calculation due to the several extrapolations involved in the evaluation of the relative enthalpy data used for the solutions is considered to be small because in each case the heat of dilution measurements were carried out to high dilution. It appears reasonable to assign an uncertainty of ±20 calories to our result.

The heat of neutralization values of Richards and Rowe[19] at 2.220 and 1.110 molal, corrected from 20 to 25° using the previously specified specific heat data, lead, respectively, to the values −13,323 and −13,329 defined calories per mole for $\Delta H^{\circ}_{\mathrm{N}}$. Pitzer[21] reported −13,367 defined calories at 25°, on the basis of a low concentration heat of neutralization measurement combined with suitable heat of dilution data. Recalculation of his result with presently accepted heat of dilution data changes it to −13,353 defined calories per mole. Rossini[22] has given an expression for $\Delta H^{\circ}_{\mathrm{N}}$ as a function of temperature based on fifty-five earlier heats of neutralization measurements together with the best currently available heat of dilution and specific heat data. For 25° his equation leads to the value of −13,320 defined calories per mole with an estimated uncertainty of ±16 calories. The precise agreement with the present value suggests that the number of determinations involved (11) minimized the effect of the uncertainties

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in the extrapolations of the early heat of dilution calculations. Lambert and Gillespie[23] used a different method of calculation, with essentially the same data as Rossini, to obtain at 20° a value differing by 44 calories from that of Rossini. They employed an extrapolation which was in principle guided by the Debye–Hückel limiting law, but the lowest concentrations for which they had data was 0.16 molal, and, as Harned and Owen[24] have pointed out, the individuality of the curves for the different 1-1 electrolyte systems involved persists well below 0.1 molal. The extrapolation of the several curves to a common point at infinite dilution is hence somewhat arbitrary rather than unique. Actually all these values are in agreement within realistic uncertainty assignments; the present value is recommended because of the over-all consistency of our results with the best available data on the individual binary solution systems involved.

In Table II is given a comparison between calculated values for the heat of neutralization and observed values obtained by appropriate interpolation of the data of Table I. The excellent accord over the entire concentration range studied shows a high degree of consistency in the several sets of actual experimental data involved, since differences in the heat of neutralization at different concentrations are faithfully reproduced, and these differences involve neither the standard heat of reaction nor any extrapolation of heat of dilution data. The direct thermochemical measurements on sodium hydroxide, hydrochloric acid and sodium chloride solutions could be expected to give accurate results. Confidence in the indirect results of Akerlof and Teare for concentrated hydrochloric acid solutions is supported by the agreement of their values for the specific heats of the solutions with those obtained by direct measurement, and by the excellent agreement of their value for the relative apparent molal enthalpy at three molal with the value given by Sturtevant. These observations, together with the agreement of Table II, show that a remarkable accuracy was achieved by Akerlof and Teare[12] in their electromotive-force study, and re-emphasize the utility of the electromotive-force method in suitable cases.

TABLE I

EXPERIMENTAL VALUES FOR THE HEAT OF NEUTRALIZATION OF SODIUM HYDROXIDE AND HYDROCHLORIC ACID SOLUTIONS AT 25°

m	$-\Delta H_N$, def. cal./mole	m	$-\Delta H_N$, def. cal./mole
16.390	20,630	8.993	16,625
15.006	19,830	6.987	15,710
13.997	19,255	6.971	15,690
13.689	19,105	4.887	14,870
12.519	18,475	3.239	14,315
10.988	17,655	3.014	14,250

TABLE II

COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF THE HEAT OF NEUTRALIZATION OF SODIUM HYDROXIDE AND HYDROCHLORIC ACID SOLUTIONS AT 25°

	$-\Delta H_N$, def. cal./mole	
m (reactants)	Observed	Calculated
3	14,245	14,250
4	14,555	14,555
5	14,915	14,910
6	15,300	15,300
7	15,715	15,720
8	16,155	16,165
9	16,630	16,645
10	17,130	17,140
11	17,655	17,655
12	18,195	18,185
13	18,735	18,715
14	19,260	19,260
15	19,825	19,830
16	20,415	20,395

Kegeles[25] has calculated the heat of neutralization using for sodium hydroxide solutions the relative enthalpy data reported by Akerlof and Kegeles[26] from amalgam cell measurements. These data lead to larger discrepancies between the observed and calculated values, averaging about 65 calories per mole and reaching a maximum of almost 200 calories per mole at 16 molal.

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