A much more comprehensive investigation of the electrical properties of the low molecular weight forms of these polymer has been carried out by other investigators in this Laboratory. Part of this has already been published,[14] and the reader is referred to this for a more detailed explanation of the electrical effects of the processes involved.

Acknowledgment.—The author wishes to express his grateful appreciation to the following: Mr. R. P. Carreker for tensile measurements, Mr. R. Cech for aid in taking motion pictures, Mr. S. I. Reynolds and Miss V. G. Thomas for the electrical measurements, and to Dr. A. M. Bueche for much helpful discussion during the course of the investigation.

SCHENECTADY, N. Y.

RECEIVED APRIL 18, 1951

(14) S. I. Reynolds, V. Thomas, R. M. Fuoss and A. H. Sharbaugh, THIS JOURNAL, **73**, 3714 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Evidence on the Elementary Reactions of Halogens Activated by Radiative Neutron Capture in Ethyl Halides and in Hydrocarbons[1]

BY SULAMITH GOLDHABER AND JOHN E. WILLARD

The organic yields (*i.e.*, fraction of nuclear events resulting in organic compound formation) of the radiative neutron capture reactions of the halogens in purified ethyl halides have been determined in the liquid and solid state, in the presence of scavengers for thermal atoms, and in hydrocarbon solvents. Among the important results are: (1) both the organic and inorganic yields of the bromide (and possibly also the iodide and chloride) are due in part to hot processes and in part to thermal processes; (2) the organic yields decrease in the order iodide, bromide, chloride; (3) the organic yields of the bromide and iodide increase with dilution with hexane; (4) the organic yields of dilute solutions of iodine or ethyl iodide appear to increase with increasing chain length of the hydrocarbon solvent from pentane to octane; (5) the organic yield of the iodide is the same in the solid phase as in the liquid phase whereas the yields of the bromide and chloride are much higher in the solid. The results have been interpreted in terms of the relative probability of nine possible competing types of elementary reactions. It is suggested that the *density* of radical production in the volume element where the tagged atom loses its energy may be a controlling factor in some cases and that the activation energy for thermal reaction with molecules of the medium may be so in other cases.

The purpose of this work was to obtain further evidence on the nature of the energy transfer processes and elementary reactions which lead to stable compounds of halogen atoms which have been activated by radiative neutron capture[2] in liquid and solid organic media.

Experimental

Purification of Reagents.—The ethyl halides and the hydrocarbons used in this work were obtained from the Eastman Chemical Co. and the Matheson Chemical Co. Impurities (presumably unsaturated compounds) present in the materials as received were found to influence seriously the results of the radiative neutron capture experiments. Except as noted below the reagents were therefore purified by prolonged vigorous mechanical stirring with successive portions of 100% sulfuric acid until no further coloration developed in the acid. After this treatment they were washed with sodium carbonate solution and with water, dried with Mallinckrodt Analytical Reagent anhydrous magnesium sulfate, and fractionally distilled through a 12″ Vigreux column, a 65% middle cut being retained.

Ozonization was used as a second method of removing unsaturated compounds from ethyl bromide. Oxygen containing about 5% ozone was bubbled through the liquid for an hour and the latter was then washed with aqueous sulfite solution to hydrolyze ozonides and remove the products of the hydrolysis. Drying and fractional distillation was carried out in the same manner as following the sulfuric acid treatment.

The concentrated sulfuric acid wash of ethyl chloride was effected by bubbling the halide gas through a 22-inch column of the acid. In other experiments the ethyl chloride purification consisted of illumination in the presence of bromine at 0° with a 1000-watt lamp, washing, drying and distillation. In some cases phosphorus pentoxide was used for the drying. The ethyl iodide was illuminated with a 1000-watt lamp in the presence of dissolved iodine, washed, dried and fractionally distilled.

Neutron Irradiations.—All the liquid phase neutron irradiations were carried out at 0° (because of the low boiling points of some of the samples) with the organic liquid in the annular space between the two walls of a soft glass vessel shaped like a wide-mouthed dewar flask and provided at the top with tubes for filling and emptying. During irradiations the vessel was surrounded by 10 l. of ice and water and an Sb–Be photoneutron source was inserted in the center tube, which was filled with water. The source contained about 3 curies of Sb^{124} and gave about 6×10^6 neutrons per sec. The time of irradiation was usually less than an hour for chlorine and iodine activation (Cl^{38} and I^{128}) and about 5 hours for bromine activation (Br^{80} (4.4 hr.)). For irradiations at liquid air temperatures the organic liquid was contained in a quartz flask, immersed in liquid air in a dewar flask which was surrounded with water. The Sb–Be source was placed in the water close to the dewar.

Extraction and Counting.—Following neutron exposure the irradiated solutions were extracted with water 0.1 *M* in sodium sulfite and 0.1 *M* in sodium halide. Except in the case of ethyl chloride elemental halogen was added to the organic liquid before removal from the irradiation vessel since it was found that this removed activity which had been picked up by the walls. In all cases the walls were rinsed with fresh extracting solution. Several counts taken on extracting solution rinses and on rinses made with concentrated caustic solution indicated that loss to the walls introduced negligible error in the final results. All experiments with bromides and chlorides were done in dim red light to preclude photochemical reaction.

The methods of counting and calculating the results were similar to those described earlier[2] except for the ethyl chloride experiments when counting was done at 0° with a hydrogen or helium filled Geiger–Muller tube with external quenching circuit.

The sum of the measured counting rates of the aqueous and organic fractions obtainable with the Sb–Be source was of the order of 500 c./m. in the case of the ethyl chloride experiments, and the experiments with very dilute solutions of the halides in hydrocarbons. Much higher rates were obtainable with the pure ethyl bromide and ethyl iodide. The standard deviation of the counting measurements was about ±1% with the pure ethyl bromide and iodide and

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(1) Presented before the Division of Physical and Inorganic Chemistry at the April, 1951, Meeting of the American Chemical Society.

(2) For a description of such processes and references to related work see S. Goldhaber, R. S. H. Chiang and J. E. Willard, THIS JOURNAL, **73**, 2271 (1951).

about ±3% with the ethyl chloride and dilute solutions of halides.

Results

Organic Yields from Pure Ethyl Halides.—Table I gives results of the radiative neutron capture experiments with pure ethyl halides. Individual experimental values are given in order to show the reproducibility attainable with the experimental techniques used. The significant conclusions to be drawn from these data are: (1) The organic yield in the liquid state at 0° increases in going from the chloride to the bromide to the iodide; (2) the organic yields of the chloride and the bromide are much greater in the solid at −190° than in the liquid at 0°, but the yield for the iodide does not change with this change in conditions; (3) the organic yield for pure liquid ethyl bromide is much lower than that reported in the literature for material presumably not subject to special purification. We have found yields similar to the literature value when using commercial ethyl bromide without special purification.

TABLE I

ORGANIC YIELDS OF THE CHEMICAL REACTIONS RESULTING FROM RADIATIVE NEUTRON CAPTURE BY THE ETHYL HALIDES

Compd.	Single expts., 0°	Average, 0°	Single expts. −190°	Average, −190°	Lit. values, room *T*
C_2H_5Cl	22.8[a]	23	59[b]	62	
	23.0[a]		65[b]		
C_2H_5Br	32.0[c]	32	78[c]	77	75[3,4]
	32.4[c]		75[c]		
	32.2[d]				
	32.0[d]				
C_2H_5I	40.8	40	42	41	37 ± 5[3]
	41.3		40		41 ± 4[5]
	40.0		40		
	39.0				

[a] Purified by photobromination. [b] Purified as gas by bubbling through sulfuric acid. [c] Purified by sulfuric acid washing. [d] Purified by ozonization.

Organic Yields from Ethyl Bromide and Iodide in the Presence of Scavengers for Thermal Atoms.—Figure 1 shows that about 0.5 mole % of elemental bromine present in ethyl bromide or 0.5 mole % of elemental iodine present in ethyl iodide during neutron irradiation reduces the organic yield by about 20% of its value for the pure liquid but that a further eightfold increase in the halogen concentration reduces the yield relatively little. It seems probable that the part of the organic yield which is not sensitive to added halogen results from combination of the tagged atoms with organic radicals immediately after the atoms have cooled and before they have had opportunity to diffuse about in the system as thermal atoms. It likewise seems probable that that part of the organic yield which is sensitive to added halogen results from combination of tagged atoms with radicals to which they diffuse as thermal atoms. Added halogen can compete with the latter process by removing the radicals and by exchanging with the thermal atoms.

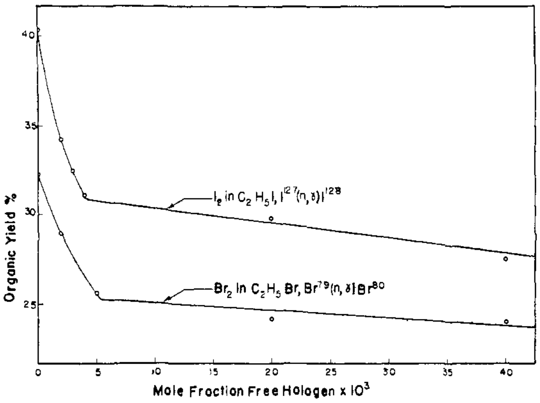

Fig. 1.—Relation between concentration of elemental halogen and the organic yield of halogen activated by radiative neutron capture in ethyl bromide and ethyl iodide.

α,β-Dibromoethylene has been shown to be an excellent scavenger for thermal bromine atoms but does not react with bromine molecules.[6] We have found that when it is present at 0.1, 0.2 or 1 mole % in ethyl bromide during neutron bombardment the organic yield is 60%, rather than 32% as observed for pure ethyl bromide. This increase is probably due to the fact that all those bromine atoms which enter either organic or inorganic combination by thermal processes in pure ethyl bromide are fixed in organic combination by the dibromoethylene. Table II gives estimates, based on this result and the data of Fig. 1, for the fraction of the atoms activated by radiative neutron capture in pure ethyl bromide and iodide which enter stable combination by different types of processes.

TABLE II

PERCENTAGES OF THE ACTIVATED ATOMS WHICH REACT BY "HOT" AND BY THERMAL PROCESSES FOLLOWING RADIATIVE NEUTRON CAPTURE BY THE HALOGEN IN PURE ETHYL BROMIDE AND IN PURE ETHYL IODIDE

	In C_2H_5Br, %	In C_2H_5I, %
Organic combination by "hot" processes	25	29
Inorganic combination by hot processes	40	
Organic combination by thermal processes	7	11
Inorganic combination by thermal processes	28	

Organic Yields in Hydrocarbon Media.—Because of its significance[7,2] as a means of revealing types of energy transfer between highly energetic atoms and molecules more information had been sought on the organic yield of "hot" halogen atoms in hydrocarbon media. The data obtained lead to the following conclusions. (1) The organic yield of (*n*,γ) activated iodine from 0.2 mole % iodine in hydrocarbons increases with chain length from about 30% in *n*-pentane to 40% in *n*-octane, while for ethyl iodide at approximately the same concentrations it is in all cases higher and increases

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(3) W. F. Libby, *Science*, **93**, 283 (1941).

(4) W. H. Hamill, R. R. Williams, Jr., H. A. Schwarz and E. E. Voiland, Univ. of Notre Dame, Radiation Chemistry Project report, March 1, 1951.

(5) P. F. D. Shaw and C. H. Cellie, *J. Chem. Soc.*, 1217 (1949).

(6) W. H. Hamill, R. R. Williams, Jr., and H. A. Schwarz, THIS JOURNAL, **72**, 2813 (1950).

(7) L. Friedman and W. F. Libby, *J. Chem. Phys.*, **17**, 647 (1949).

in a similar manner but from about 44 to 53%[8]; (2) the organic yield of (n,γ) activated halogen observed for pure ethyl bromide and pure ethyl iodide increases when they are diluted with n-hexane, the change being from 32 to 47% when ethyl bromide is diluted to 0.3 mole %; (3) the organic yield for the isomeric transition reaction (Br^{80} (4.4 hr.) $\rightarrow$ Br^{80} (18 min.)) present as ethyl bromide is increased from 43 to 56% when the ethyl bromide is diluted to 0.05 mole % with hexane. In both the (n,γ) and isomeric transition types of reaction the organic yield increases progressively with intermediate values of the hexane dilution in the range covered.

The above conclusions are qualitative in nature because the low counting rates from dilute solutions resulted in high statistical error. The trends with dilution and hydrocarbon chain length are difficult to explain. The possibility that they are due to impurities remaining even after the extensive stirring with sulfuric acid, washing and distillation probably cannot be wholly excluded. Less rigorously purified reagents gave higher organic yields which, however, fell in the same order. Regardless of the explanation of the trends, the data confirm the fact that high energy iodine atoms can enter organic combination in hydrocarbon media.

It has been reported[9] that the organic yield of bromine from the (n,γ) reaction on the members of the homologous series of alkyl bromides from methyl bromide to hexyl bromide increases with increasing chain length and tends to be higher for chains with an odd number of carbon atoms.[9]

Discussion

Types of Elementary Reactions Possible.—A halogen atom which undergoes radiative neutron capture emits one or more gamma rays. Both the available physical evidence on the gamma ray spectra[10] and the chemically observed low organic yields from the bombardment of gaseous halides[11,3] are consistent with the conclusion that the great majority of such atoms receive a recoil energy far in excess of chemical bond energies. These atoms must break away from their parent combination and eventually lose their excess energy by collisions with molecules of the medium. Such a "cooled" atom may then enter stable combination by a process which occurs before it has opportunity to diffuse about in the system as a thermal atom (designated here as a "hot" process) or by a thermal process after diffusion. Among the processes of each type which may occur in an alkyl halide medium are the following.

Hot processes which may lead to organic combination: (1) A cooled tagged atom may combine with a radical which it has formed by a nearly head-on billiard-ball collision with the halogen atom of an alkyl halide molecule. The inactive halogen atom is knocked out of the solvent cage and the tagged atom remains with the radical. Although this is the most commonly used mechanism in the discussion of reactions activated by the (n,γ) process and has been the basis for theoretical treatments of these phenomena[12] it seems to require a rather improbable event, and a growing amount of evidence suggests that it may be of minor importance. This evidence includes (a) the production of organic products which could only be formed by multiple bond rupture[2,13]; (b) the observations in the work of this paper and earlier[2,11b] that organic yields may be due in part to thermal processes, and inorganic yields in part to hot processes; (c) the substitution of hydrogen atoms by bromine and iodine atoms activated by the (n,γ) process, observed in the work of this paper and earlier.[7]

(2) The tagged atom may combine with a radical which it has formed in the cooling process (by an act other than described in (1)) and which it encounters after it has lost sufficient energy to form a stable compound and before it has had opportunity for competitive thermal reactions with other species in the system.

Reactions of type 2, like those of type 1, would not be affected by the addition of scavengers for thermal atoms. Because they can include reactions of the tagged halogen with radicals formed by the breaking of carbon–carbon and carbon–hydrogen bonds, they may produce tagged organic compounds which could not be produced by reactions of type 1. Such compounds can be identified by fractionation with carriers.

(3) The tagged atom may react with a molecule by a high activation energy process just before the atom has reached thermal energies. For example:

$$C_2H_5X + X^* \longrightarrow C_2H_5X^* + X \text{ or}$$
$$C_2H_5X + X^* \longrightarrow CH_3X^* + CH_2X$$

in a step analogous to a Walden inversion. Such processes have been termed "hot radical reactions."[4]

Hot processes which may lead to inorganic combination: (4) The tagged atom may react with a halogen atom instead of an organic radical by a process similar to 2 above.

(5) The tagged atom may form a halogen or hydrogen halide molecule by a "hot radical reaction" similar to type 3 above:

$$C_2H_5X + X^* \longrightarrow C_2H_5 + XX^* \text{ or}$$
$$C_2H_5X + X^* \longrightarrow C_2H_4X + HX^*$$

Thermal processes which may lead to organic combination: (6) A thermalized tagged atom may combine with a radical which it has formed in the cooling process but which it encounters again only after many thermal collisions with the other species in the medium.

(7) A thermalized tagged atom may take part in a reaction of the type

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[8] The hydrocarbons used in the experiments with dissolved *elemental* iodine were not rigorously purified whereas those used in the experiments with ethyl halides were purified. This difference is not a satisfactory explanation of the difference in organic yield since other experiments indicate that the impurities *raise* rather than lower the organic yield.

[9] A. S. Karamyan, *Doklady Akad. Nauk. U. S. S. R.*, **69**, 787 (1949); *Nuclear Science Abstracts*, **4**, 2719 (1950).

[10] B. Hamermesh, *Phys. Rev.*, **80**, 415 (1950).

[11] (a) H. Suess, *Z. physik. Chem.*, **B45**, 297 (1940); (b) R. R. Williams, Jr., and W. H. Hamill, *J. Chem. Phys.*, **18**, 783 (1950); (c) S. Wexler and T. H. Davies, Brookhaven National Laboratory Report No. C-7 (1948).

[12] (a) W. F. Libby, THIS JOURNAL, **69**, 2523 (1947); (b) J. M. Miller, J. W. Gryder and R. W. Dodson, *J. Chem. Phys.*, **18**, 57 (1950).

[13] E. G. Bohlman and J. E. Willard, THIS JOURNAL, **64**, 1342 (1942).

$$C_2H_5X + X^* \longrightarrow C_2H_5 + X^*X \text{ or}$$
$$C_2H_5X + X^* \longrightarrow C_2H_4X + HX^*$$

where the XX* or HX* molecule is caged with the radical formed and undergoes the reverse reaction with it to form tagged $C_2H_5X^{*2}$.

Thermal processes which may lead to inorganic combination: (8) The tagged atom may react by a process similar to type 6 but involving reaction with an inorganic radical (halogen atom).

(9) The tagged atom may undergo a thermal reaction of the type:

$$C_2H_5X + X^* \longrightarrow C_2H_4X + HX^* \text{ or}$$
$$C_2H_5X + X^* \longrightarrow C_2H_5 + X^*X$$

where the inorganic product escapes from the cage without back reaction.

The nine possibilities listed above include all the types of reaction which appear to have a possibility of being important in the work reported in this paper. Their relative importance must depend on the physical properties of the molecules such as the masses and configurations of the atoms and groups which determine the nature of the energy transfer processes responsible for the moderation of the hot atom. It must also depend on the chemical nature of the medium and in particular on the relative activation energies of various competing thermal processes.

Although ions and radicals are produced in large numbers by gamma, beta and fast neutron radiation during the neutron bombardments of the systems investigated in this work, the evidence seems to indicate that fragments of this origin do not control the organic yield of the tagged atoms. This is certainly true for that portion of the organic yield which is relatively insensitive to elemental halogen concentration (Fig. 1), since the elemental halogen would reduce the concentration of such radicals very greatly and at the same time fix the tagged atoms in inorganic combination by the reaction $X^* + X_2 \rightarrow X_2^* + X$. It is more difficult to be certain about that portion of the organic yield which is sensitive to halogen concentration. We have recently found that the total organic yield from ethyl iodide is the same when irradiation is at a flux of 10^7 neutrons/cm.^{2}/sec. in the thermal column of the Argonne National Laboratory pile as it is at a flux of about 10^4 neutrons/cm.^{2}/sec. obtained with an Sb–Be source. The fact that very low organic yields are observed in the gas phase may also be evidence that the combination of tagged atoms with radicals produced by the general radiation in the system is negligible.

Energy Loss in Liquid and Solid Media.—A halogen atom with several hundred or thousand kcal./mole of kinetic energy in a liquid or solid medium collides with molecules which are packed relatively tightly together and backed by a thick wall of other molecules. In such a collision it is to be expected that not only the molecule which is struck may have bonds broken but that adjacent molecules may also be fragmented or activated, forming *a small volume element in the liquid with a very high density of radicals.* If we consider hot atoms of equal size and energy in different media we may expect the local density of radicals formed to be greatest in media with: (a) high density and little free space for the hot atoms to pass between molecules without fracturing them; (b) long intertwined molecules which cannot be pushed apart or roll over each other easily. In the case of hot atoms of the same energy but different size in the same medium the smaller atoms would be expected to have a higher probability of passing between molecules without fragmenting them and therefore produce a lower density of radicals. The relative masses of the hot atoms and the atoms and molecules of the medium will affect the energy loss in a complex manner interrelated with the other variables.

The *density of radicals* in the small volume element where the tagged atom reaches thermal energies may be important in determining whether the atom will combine with a radical or undergo a competitive reaction with a molecule.

Relative Organic Yields of Alkyl Halides.—The decreasing organic yields observed for the series ethyl iodide, ethyl bromide, ethyl chloride (Table I and Fig. 1) are consistent with the effects of radical density and activation energy of thermal reactions considered above. Essentially all thermalized tagged iodine atoms will be expected to react with radicals formed by the hot atom because the high activation energy for reaction with solvent molecules to form HI or I_2 will prevent these reactions from competing effectually. The organic yield is therefore dependent only on the hot processes and on the relative probability of reaction with different types of *radicals* in thermal processes.

The relatively low organic yield for ethyl chloride may be attributed to the fact that the reaction of chlorine atoms with ethyl chloride to form HCl is exothermic and probably has a very low activation energy which allows it to compete favorably with steps leading to combination with radicals. The case of the bromide is intermediate between that of the iodide and chloride.

The data of Fig. 1 and Table III indicate that the organic yield from hot processes (*i.e.*, the yield in the presence of added free halogen) is lower for ethyl bromide than ethyl iodide. This may be due to the fact that the radical density around the tagged atom is less in ethyl bromide and so reactions of type 5 are competitively favored, and/or to the lower energy required for reactions of type 5 in the bromide case. In accordance with this trend one would expect that the hot process organic yield for pure ethyl chloride would be still lower. Although this hot yield has not been determined it cannot be greater than the total organic yield (23%) which is less than the hot yield (25%) of ethyl bromide. The number of molecules per cc. in ethyl bromide is approximately the same as that in ethyl chloride although the molecular weight is 70% greater. This fact, as well as the larger size of the hot bromine atom, may lead to a higher radical density in the volume where the bromine atom loses its energy.

It seems probable that the reduction in organic yield of ethyl chloride by addition of free halogen will be found to be less than in the case of the bromide and iodide because of the ability of HCl 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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MADISON, WISCONSIN RECEIVED JULY 16, 1951

[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).