4.4 hr. activities present at the end of 180 min. neutron irradiations of the organic bromides were determined with the aid of decay curves taken on the aqueous and organic fractions. Immediately after such an irradiation, the disintegration rate due to the 18 min. isomer formed by the (n,γ) process is about ten times that due to isomeric transition. Hence the observed organic yield of the 18 min. species could not be greatly influenced by the contribution from the isomeric transition process unless the latter gave a distribution widely different from the former. The organic yield of Br^{80} (18 min.) due to the isomeric transition of the Br^{80m} in the chemical forms in which it exists in *n*-propyl bromide which has been irradiated with neutrons for 180 min. was determined by allowing the samples to stand for 180 min. before extraction and then determining the decay curves of the aqueous and inorganic fractions. The initial points showed only slight evidence of a different distribution of the 18 min. activity from the isomeric transition than the 4.4 hr. activity from the (n,γ) process.

Test of Isomer Effect

***n*-Propyl Bromide.**—In eleven determinations which were carried out of the organic yield of the 18 min. isomer, and nine of the 4.4 hr. isomer, from the neutron irradiation of purified *n*-propyl bromide we have obtained yields of 31.7 ± 0.9% and 32.5 ± 1.1%, respectively. The results are in good agreement with those of Libby and co-workers[5,6] and indicate that there is no significant isomer effect in pure *n*-propyl bromide. Other experiments gave identical organic yields for the two isomers at each of a series of bromine concentrations in *n*-propyl bromide up to 8×10^{-2} mole fraction, proving that the "scavenger"[10-13] effect is the same for the two species.

In contrast to the above results, experiments in which commercial *n*-propyl bromide (Eastman white label) was used without further purification always gave a higher organic yield for the longer lived isomer, in agreement with the results of Capron and co-workers.[1,3,4] Typical values were 45 and 66% for the 18 min. and 4.4 hr. isomers in the absence of added bromine and 38 and 44% when 1×10^{-3} mole fraction of bromine was present during irradiation.

Bromoform.—Purified degassed bromoform irradiated with neutrons in sealed quartz tubes gave organic yields of 65.6 ± 1.2% (8 detn.) for the 18 min. isomer and 66.1 ± 1.1% (4 detn.) for the 4.4 hr. isomer. The same yields were obtained with 20, 180 and 720 min. irradiation times. Purification was accomplished by adding Br_2, illuminating for eight hours with a 1000-watt lamp, washing with sulfite solution, drying, fractionally distilling under reduced pressure and degassing on a vacuum system.

When Eastman white label bromoform, which contains diphenylamine as stabilizer, was used, either as received or after fractional distillation in a Vigreux column, it gave organic yields of 76 and 94% for the 18 min. and 4.4 hr. isomers. Degassed samples of this impure material gave results similar to those irradiated in the presence of air.

Bromobenzene.—Attempts to obtain reproducibly pure bromobenzene for investigation of isomer effects have not yet been successful. Mr. Robert Chiang and Mr. James Evans of our laboratory have found that slight variations in a variety of apparently rigorous procedures for the purification of C_6H_5Br yield samples which give organic yields varying from 47 to 88%. This makes it seem probable that the apparent isomer effect obtained from this compound,[3] like that from the propyl bromides and bromoform, was due to impurities. The "scavenger" effect on this compound is very great; the organic yield with 3 mole % of added Br_2 present is only about 29%. One or more of the organic products of the (n,γ) process on C_6H_5Br in the absence of Br_2 scavenger is slowly hydrolyzable by the aqueous extracting solution, which further complicates the determination of precise organic yields.

Absence of Neutron Energy Effects

Capron and co-workers suggested that neutron energies[3] and neutron intensities[1] may affect the organic yields obtained from the (n,γ) process. Such effects have not been observed by other workers using highly purified samples. We obtain 32 ± 2% as the organic yield for highly purified *n*-propyl bromide with samples exposed to Sb–Be photoneutron sources of different intensities, and with samples exposed at different intensities and different degrees of neutron moderation in the CP3′ nuclear reactor at the Argonne National Laboratory. These values agree with those obtained elsewhere at different fluxes and degrees of moderation using a cyclotron[5] as a neutron source and using a Po–Be neutron source.[6] We likewise have found the organic yields from bromoform to be independent of whether a Sb–Be photoneutron source was used or a Ra–Be source with a paraffin moderator duplicating that described by Capron and co-workers. In a variety of other studies on activation by radiative neutron capture[8-13] we have never observed effects due to neutron energies or neutron intensities.

Apparent Isomer Effect Following High γ-Dosage

It has been firmly established that wide variations of γ-ray intensity and total γ-dose during neutron irradiation do not alter the organic yields obtained from alkyl halides[6,11,12] if these variables are within the ranges normally prevailing in studies of the chemical effects of the (n,γ) process. This is a very important fact because it indicates[11] that the chemical fate of the recoil atom must be determined in or near the spot where it is born and is not affected by radicals generated elsewhere in the solution.

Just as initially impure organic bromides show an apparent isomer effect on organic yields from the (n,γ) process, it might be expected that sufficiently prolonged radiolysis of some compounds would produce impurities with which the Br_2 and/or HBr formed by the Szilard Chalmers process could react to give fictitiously high organic yields. We have found that the minimum γ-ray dosage required to show the effect for the 4.4 hr. species in air-free *n*-propyl bromide is about 20,000 roentgens.[14] Purified degassed *n*-propyl bromide which gave organic yields of 33.7 and 32.6% (single detn.) for the 18 min. and 4.4 hr. isomers after 4 hr. irradiation with a 5 curie Sb–Be photoneutron source at a distance of 4 cm. through paraffin gave very little change in the 18 min. yield up to 132 hr. while the 4.4 hr. yield increased to 45% at 24 hr., 53% at 40 hr. and 73% at 132 hr. Corresponding yields of Br^{82} (36 hr.) determined for 40, 80 and 132 hr. irradiation were 67, 88 and 90. A similar sample subjected a γ-irradiation of 3×10^6 r. from a 40 curie Co^{60} source just prior to a 4 hr. irradiation with the Sb–Be source gave organic yields of 44 and 58% for the 18 min. and 4.4 hr. isomers.

Conclusion.—There appears to be no basis for believing that an isomer, isotope, or neutron energy effect is important in determining the organic yields of bromine in pure liquid alkyl bromides, although apparent isomer effects due to the reaction of stabilized products of the (n,γ) process with impurities may be observed easily.

Acknowledgment.—This work was supported in part by the Atomic Energy Commission and in part by the University Research Committee with funds supplied by the Wisconsin Alumni Research Foundation.

---

[14] We have investigated this "secondary radiation effect" on the organic yields of the three bromine nuclides and expect to report the detailed results later.

DEPT. OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON 6, WISCONSIN

Heats of Reaction of Sodium and Potassium with Water and the Standard Heats of Formation of Aqueous Sodium and Potassium Hydroxides at 25°

BY EUGENE E. KETCHEN AND W. E. WALLACE

RECEIVED APRIL 10, 1954

The standard heats of formation of aqueous sodium and potassium hydroxides are of considerable thermochemical significance since they are employed in establishing much of the thermochemical data for other sodium and potassium compounds. Several years ago we published[1] data for the heats of reaction of sodium and potassium with water, from which the heats of formation of the hydroxide could readily have been calculated. Being interested in the other aspects of the data we did not make this simple calculation and furthermore failed[2] to label our data sufficiently well to enable other interested individuals to utilize the results in making this or other calculations. The purpose of this note is to clarify the labeling of our earlier results and to use them to compute the heats of formation of NaOH and KOH at infinite dilution in water at 25°.

For the reaction[3] metal(s) + $\infty H_2O(l) \rightarrow$ metallic hydroxide (∞H_2O) + $^1/_2H_2(g)$, $\Delta E_{298.16} = -44{,}350$ and $-47{,}190$ cal. for sodium[4] and potassium, respectively. These are the means of the experimental quantities, a constant volume calorimeter having been used.[1] Correcting to constant pressure and using $-68{,}317$ cal. as the standard heat of formation of water[5] at 25°

$$Na(s) + {}^1/_2H_2(g) + {}^1/_2O_2(g) + \infty H_2O(l) \longrightarrow NaOH(\infty H_2O) \quad \Delta H_{298.16} = -112.37 \text{ kcal.};$$

$$K(s) + {}^1/_2H_2(g) + {}^1/_2O_2(g) + \infty H_2O(l) \longrightarrow KOH(\infty H_2O) \quad \Delta H_{298.16} = -115.21 \text{ kcal.}$$

The corresponding data given in the National Bureau of Standards compilation[5] are -112.23 kcal. for sodium and -115.00 kcal. for potassium.

---

(1) E. E. Ketchen and W. E. Wallace, THIS JOURNAL, **73**, 5810 (1951).

(2) We are grateful to Professor Leo Brewer of the University of California for calling attention to this.

(3) Corrections to infinite dilution were made using data published by J. H. Sturtevant, THIS JOURNAL, **62**, 2276 (1940) for sodium hydroxide and by H. S. Harned and M. S. Cook, *ibid*, **59**, 496 (1937) for potassium hydroxide.

(4) In reference (1) Table I contains a typographical error. One of the individual heats of reaction of sodium with water reads $-44{,}400$ cal. instead of the correct value $-44{,}460$ cal.

(5) "Selected Values of Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA

The Behavior of 1,2-Diketones at the Dropping Mercury Electrode: an Addendum

BY NELSON J. LEONARD, H. A. LAITINEN AND EDWARD H. MOTTUS

RECEIVED MAY 12, 1954

In the paper by Schwabe and Berg,[1] which reached us after the publication of our article[2] on the polarographic reduction of 1,2-diketones,[3] the reduction of camphorquinone was described as a two-electron process. Since our conclusion that the reduction involved a one electron process was based in part upon the favorable comparison of calculated (for camphorquinone in 50% isopropyl alcohol–water) and observed (for camphor in 96% ethyl alcohol–water)[4] diffusion coefficients, it seemed desirable to examine more critically the basis of this comparison. The viscosity of isopropyl alcohol–water mixtures passes through a maximum[5] near the 50% composition which was used as the solvent in our experiments and thus chances to be more than twice that of 96% ethanol and about three times that of water. A comparison[6] of the polarographic wave heights of camphorquinone in water and in 50% isopropyl alcohol–water led to reasonable values of a diffusion coefficient only if n were taken equal to 2. In water, if n were assumed equal to 1, an improbably high value (34×10^{-6} cm.^{2}/sec.) was obtained.

Apparently, therefore, the reduction of camphorquinone is a two electron process,[1] and presumably this is so for the other members of the series of 1,2-diketones[2,7] which were found to be reducible at the dropping mercury electrode.[8] This conclusion does not affect the half-wave potentials as reported in our previous paper and therefore does not alter the order of reducibility of the 1,2-diketones. It will be noted that Schwabe and Berg[1] proposed a mechanism for the initial reduction step identical with that which we suggested.[9] The preferred fate of the intermediate radical, if such is indeed formed, would then require rapid absorption of the second electron and proton. It remains true that any mechanistic sequence proposed for the polarographic reduction must take into account the steric factors[2] in the acyclic and cyclic 1,2-dicarbonyl systems.

---

(1) K. Schwabe and H. Berg, *Z. Elektrochem.*, **56**, 952 (1952).

(2) N. J. Leonard, H. A. Laitinen and E. H. Mottus, THIS JOURNAL, **75**, 3300 (1953).

(3) See also S. Wawzonek, *Anal. Chem.*, **26**, 65 (1954).

(4) "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., Vol. 5, 1929, p. 74.

(5) J. Traube, *Ber.*, **19**, 871 (1886), found the following viscosities: at 20°, 10% (wt. % *i*-PrOH in H$_2$O), 16.10; 50%, 38.17; 100%, 25.43; at 30°, 10%, 12.30; 50%, 25.58; 100%, 18.78 millipoises.

(6) Experiments by Mr. R. A. Osteryoung in this Laboratory.

(7) See also R. Pleticha, *Chem. Listy*, **46**, 69 (1952); *ibid.*, **47**, 43 (1953).

(8) Examination of other polarographic data accumulated in this Laboratory in July, 1950, when some of our early measurements were made, cast doubt upon the calibration of the recorder as to current sensitivity. In particular, this affected the value of camphorquinone in the same direction as did the viscosity.

(9) Figure 1D, in ref. 2.

THE NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

Regularities in the Densities of Dilute Solutions of Some Monochlorobenzotrihalides[1]

BY RICHARD H. MYERS, MARCUS E. HOBBS AND PAUL M. GROSS

RECEIVED APRIL 12, 1954

In the measurement of the electric moments of some monochlorobenzotrihalides, using dilute benzene solutions, certain regularities were noted in the ratio, $\Delta d/f_2$, of the density increment to the mole fraction of the solute. Since these regularities may be of significance in similar or other related investigations the results of the density determinations are reported below.

Experimental

The physical constants determined for the several compounds used in the investigation are given in Table I where $d^{30}{}_4$ is the density, n^{30}D the refractive index, f.p. the freezing

---

(1) Taken in part from the Ph.D. Thesis of Richard H. Myers, Duke University.