[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

# The Iodide Ion Exchange Reaction with 2-Haloethyl Alkyl Ethers and *n*-Butyl Bromide[1]

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RECEIVED OCTOBER 19, 1953

Specific reaction rates have been determined for the potassium iodide exchange reaction in acetone with *n*-butyl bromide and 2-bromoethyl-*n*-butyl ether at 15, 25 and 35°, and with 2-bromoethyl methyl ether at 15 and 25°. It is indicated that the relative slowness of reaction of the $\beta$-halogen ethers results from an increased energy of activation. Reaction rates of 2-chloroethyl ethyl ether at 35° and somewhat impure 2-bromoethyl ethyl ether at 25° have been measured also.

The halogen atom in $\beta$-halogen ethers seems to be less reactive in displacement reactions than does the halogen atom in normal alkyl halides and much less reactive than that in an $\alpha$-halogen ether.[2-5]

The present communication reports the results of kinetic measurements of the iodide replacement reaction in acetone, $RX + KI = RI + KX$, for several 2-haloethyl alkyl ethers and for *n*-butyl bromide, which was used for comparison.

Methods used for following this exchange reaction in acetone have been largely volumetric ones involving determinations of the concentration of unreacted iodide ion, using either an Andrews titration[6] or the Lang method,[7] with or without the removal of acetone, which decidedly interferes with visual detection of the end-point. Several years ago a study of various methods of determination of iodide ion was made and a potentiometric titration using potassium iodate finally employed.[8] Conductometric methods have been used recently[9] but also have been tried without success.[8a]

The authors experimented with visual titration procedures involving the Andrews method with potassium iodate, the Lewis method with ceric sulfate,[10] and the Berg procedure,[11] all for the determination of the unreacted iodide ion in the presence of acetone. Of these, the Lewis procedure with proper modifications would seem the best, although none possessed the convenience and exactness desired. A rapid potentiometric procedure using potassium iodate eventually was devised.

## Experimental[12]

Temperatures were held to ±0.01° for each series of measurements.

**Chemicals.**—Merck reagent grade potassium iodide and potassium iodate were recrystallized from water and dried *in vacuo* at 132°.

The acetone used was Merck reagent grade, purified by the method of Conant and Kirner.[6] It had a boiling point of 55.9° (755 mm.).

Eastman Kodak Co. *n*-butyl bromide was washed with water, extracted with chilled concentrated sulfuric acid, then washed with water several times. It was dried over calcium sulfate, filtered and distilled. That portion boiling at 100.1° (753 mm.) was used; $n^{25}{}_D$ 1.4374, $n^{20}{}_D$ 1.4399, $d^{25}{}_4$ 1.2678.

Eastman Kodak Co. 2-bromoethyl ethyl ether was fractionated and the portion boiling at 35.9–36.4° (25.5 mm.) was used for the rate measurement[13]; $n^{25}{}_D$ 1.4420. A yellow color (iodine) formed slowly when this compound was treated with potassium iodide in acetone, owing to the presence of a small amount of ethylene bromide. It was found impracticable to remove this impurity (estimated at 1%) completely.

2-Bromoethyl *n*-butyl ether was made by a modification of the procedure of Palomaa and Kenetti.[2] The product was fractionated carefully and a sample boiling at 59.5–59.7° (13 mm.) collected for use in the rate measurements; $n^{25}{}_D$ 1.4445, $d^{25}{}_4$ 1.2228. *Anal.* Calcd.: Br, 44.13. Found: Br, 44.17. Our density is in accord with that of Palomaa and Kennetti but not with other reported values.[14]

2-Bromoethyl methyl ether was prepared from ethylene bromohydrin, dimethyl sulfate and calcium carbonate.[15] Fractionation of the product gave a portion boiling at 40.6° (66.0 mm.) which was used for the rate measurements; $n^{25}{}_D$ 1.4417, $d^{25}{}_4$ 1.4369. *Anal.* Calcd.: Br, 57.49. Found: Br, 57.19.

The sample of $\beta$-chloroethyl ethyl ether used was prepared by M. B. Winstead, Jr., of this Laboratory from Cellosolve and thionyl chloride. It was washed with 5% sodium hydroxide solution, then with water, dried over magnesium sulfate, and fractionated; b.p. 107.1–107.4° (748 mm.), $n^{25}{}_D$ 1.4091, $n^{20}{}_D$ 1.4116.

**Procedure.**—In all the determinations of rate constants except those on 2-chloroethyl ethyl ether and the impure 2-bromoethyl ethyl ether the following procedure was used. Concentrations of potassium iodide and organic bromide were approximately 0.040 and 0.20 *M*, respectively. Weighed quantities of organic bromide were placed in 10-ml. g.s. volumetric flasks which were then tightly stoppered. In most instances the stoppers were sealed by a smear of silicone grease after the bromide had been weighed.

The flasks were then put in the constant temperature bath for 10–20 minutes to allow thermal equilibrium to be reached. Meanwhile, a bottle of the acetone solution of potassium iodide had been placed in the bath. Five-milliliter portions of the solution were withdrawn and added to the flasks, the time being noted when addition was half completed. The stopper of the flask was replaced (and in some cases smeared with the silicone grease), the contents swirled to mix the reactants and the flask allowed to remain

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[1] Abstracted from a portion of a thesis submitted by Frank B. Tutwiler in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of North Carolina, June, 1951.

[2] (a) A. Karvonen, *Ber.*, **42**, 687 (1909); (b) M. H. Palomaa and A. Kenetti, *ibid.*, **64B**, 797 (1931).

[3] W. Jacobs and M. Heidelberger, *J. Biol. Chem.*, **21**, 439 (1915).

[4] (a) P. D. Bartlett and E. S. Lewis, THIS JOURNAL, **72**, 405 (1950); (b) H. Böhme and K. Sell, *Chem. Ber.*, **81**, 123 (1948), (c) H. Mohler and J. Hartnagel, *Helv. Chim. Acta*, **25**, 859 (1942).

[5] (a) W. R. Kirner, THIS JOURNAL, **48**, 2743 (1926); (b) W. R. Kirner and G. H. Richter, *ibid.*, **51**, 3409 (1929).

[6] J B. Conant and W. R. Kirner, *ibid.*, **46**, 232 (1924).

[7] (a) I. Dostrovsky and E. D Hughes, *J. Chem. Soc.*, 161 (1946); (b) G. M. Bennett and W. A. Berry, *ibid.*, 1683 (1927).

[8] (a) H. Skolnik, A. R. Day and J. G. Miller, THIS JOURNAL, **65**, 1858 (1943); (b) K. L. Senior, R. R. Hetrick and J. G. Miller, *ibid.*, **66**, 1987 (1944).

[9] (a) A. G. Evans and S. D. Hamann, *Trans. Faraday Soc.*, **47**, 30 (1951); (b) B. Jones and D. J. Worsfold, *Nature*, **167**, 1072 (1951).

[10] D. Lewis, *Ind. Eng. Chem., Anal. Ed.*, **8**, 199 (1936).

[11] R. Berg, *Z. anal. Chem.*, **69**, 369 (1926).

[12] All temperatures are corrected.

[13] When the 2-bromoethyl alkyl ethers were boiled at atmospheric pressure, distillates which fumed in moist air (hydrogen bromide) were produced and the residue in the distillation flask turned brown, while distillation at reduced pressure usually gave non-fuming products. In none of the fuming distillates could unsaturation be detected. When they were shaken with water, solutions giving positive Schiff tests for aldehydes and ceric nitrate tests for alcohols were formed. *n*-Butyl alcohol (urethan, m.p. 57–57.5°) was isolated from one of the *n*-butyl ether distillates. The presence of 1-bromo ethers is suggested. A further study of this decomposition will be reported in a later paper.

[14] (a) R. C. Tallman, THIS JOURNAL, **56**, 126 (1934); (b) W. Chambers. *Can. J. Research* **7B**, 464 (1932).

[15] R. O. Roblin, J. P. English, Q. P. Cole and J. R. Vaughan, THIS JOURNAL, **67**, 290 (1945).

in the bath with occasional shaking. One of the 5-ml. portions of potassium iodide from the stock solution was run into a 250-ml. beaker containing 25–30 ml. of concentrated hydrochloric acid, 20 g. of ice and 25 ml. of water, set in an ice-bath. By titrating this solution potentiometrically with potassium iodate, the initial concentration of potassium iodide solution was found. The volume of organic halide was added to that of the stock solution to give the volume of the reaction mixture used in the calculations. Any volume change on mixing or during reaction was neglected.

At a given time a flask was taken from the thermostat, wiped quickly, and emptied into a 250-ml. beaker containing the hydrochloric acid solution in an ice-bath. The time was recorded at the moment of pouring. The flask was rinsed three times with water and the cold solution then titrated. The ratio of ice to water in the beaker made little difference, but it was essential to keep the mixture cold.

This reaction has been shown to be second order.[6] This was further verified by the authors in an $n$-butyl bromide experiment with varying ratios of initial concentrations of bromide and iodide. Substitution in the rate equation

$$k = \frac{1}{(a-b)t}\log\frac{x+a-b}{x} \times \frac{b}{a}$$

where $a$ and $b$ are the initial concentrations in moles per liter, of organic halide and potassium iodide, respectively, and $x$ is the concentration of potassium iodide at time $t$, gives the rate constant $k$ in liters per mole per hour. An average of $k$'s for the individual samples was taken as the specific reaction rate for that temperature.

## Results and Discussion

**Analytical Procedure.**—In the Andrews titration of iodide in the presence of acetone, if the addition of iodate proceeds fairly slowly, a strong iodine color never develops, and, no matter what the rate of addition, the end-point besides being fleeting is often considerably early. Conant and Kirner considered their analyses accurate only to about 4% and their rate constants often showed considerable variation. Senior, Hetrick and Miller[8b] noted that Andrews titrations in rather dilute solutions were not successful when followed visually but did not offer any explanation for this fact.

It is proposed that when acetone is present a high concentration of iodine is never built up unless the iodate is added all at once, since iodination of the acetone in acid solution takes place readily (though not instantaneously).[16] The liberated iodide ion is then converted back to iodine as more iodate is added, and the process continues. Thus, the final end-point in the titration is not reached when there is complete conversion to $ICl_2^-$ but when the iodine is in the form of iodoacetone. A colorless end-point is actually obtained, while in the absence of acetone the solution is amber. Even when ice is added to the beaker and it is set in an ice-bath, the end-point, determined potentiometrically, begins to fade in about 30 min. probably because of hydrolysis of the iodoacetone. The hydrolysis of $ICl_2^-$ in the regular Andrews titration takes place somewhat less readily.

The general procedure for preparing the sample for titration was adapted from that of Senior, Hetrick and Miller. A saturated potassium chloride–calomel cell and a bright platinum electrode were used. A double throw switch allowed the connection of either a Serfass titrimeter[17] or a conventional potentiometer circuit to the electrodes. In every case the initial potential after the addition of 5–10 ml. of iodate was about 0.31 v. The end-points were sharp, characterized by a rapid rise in potential to 0.52–0.57 v., the "break" being about 0.15 v. The "eye" when properly set would close for 3–10 min. Even after the solution had stood for 30–45 min. at the end-point, a few drops of iodate would bring the potential back up. The solutions had to be stirred constantly and time allowed for them to become colorless before each potential reading. The voltage would surge upward as iodate was added and not come down until all the iodine had been transformed. Under these conditions, smooth titration curves resulted. During the rate measurements usually only initial and final potential readings were taken.

In the selected experiments recorded in Table I which demonstrate the validity of the method, 25 ml. of approximately 0.0100 $N$ aqueous potassium iodide and 30 ml. of concentrated hydrochloric acid were used. The potassium iodide solution was standardized by an Andrews titration without acetone. The potassium iodide was 0.005711 $N$. Other titrations with 25 ml. of concentrated hydrochloric acid and varying amounts of water gave just as good results. Titrations with added $\beta$-halogen ethers also exhibited undisturbed end-points. Titrations of iodide with iodate without added acetone, on the other hand, show two inflection points and there is some question as to the reliability of either point.[18] The authors obtained a potential of 0.85 v. at the theoretical equivalence point without acetone, but the end-point in the titration came about 0.20 ml. too soon. Acetone seems to provide a better potentiometric end-point than there would be in its absence.

TABLE I

RESULTS OF POTENTIOMETRIC TITRATIONS OF POTASSIUM IODIDE WITH POTASSIUM IODATE

| Vol. acetone used, ml. | Water or ice g. | Obsd. end-point, ml. | Theor. end-point, ml. | Potential at end-point, v. |
|---|---|---|---|---|
| 5 | 20 (ice) | 43.74 | 43.76 | 0.53 |
| 5 | 20 (water) | 43.78 | 43.76 | .52 |
| 10 | 20 (ice) | 43.82 | 43.81 | .53 |
| 5 | 15 (ice) | 43.83[a] | 43.81 | .56 |
| 5 | 15 (ice) | 43.83[b] | 43.81 | .57 |

[a] 5 ml. of 0.040 $M$ KBr added. [b] 6 ml. of 0.040 $M$ KBr and 0.10 ml. of ethyl iodide added.

**Rate Measurements.**—Determinations in the rate of 50–70% reaction predominate as it is there that the error in $(KI)_t$ is minimized in the calculation of the rate constant. About six measurements were made on each compound. Mean deviations of the average $k$'s were 0.13–3.0% for all compounds except the $\beta$-bromoethyl ethyl ether which did not give as good results. The average mean deviation was 1.4%. Table II shows the data for two typical runs. The rates of the $\beta$-chloroethyl and $\beta$-bromoethyl ether reactions were measured by pipetting samples from mixtures made up in larger flasks, with the results shown in Table III.

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(16) H. M. Dawson, *J. Chem. Soc.*, 458 (1927).

(17) E. J. Serfass, *Ind. Eng. Chem., Anal. Ed.*, **12**, 563 (1940).

(18) (a) I. M. Kolthoff and N. H. Furman, "Potentiometric Titrations," 2nd. ed., John Wiley and Sons, New York, N. Y., 1931; (b) E. Müller and D. Junck, *Z. Elektrochem.*, **31**, 200 (1925).

TABLE II

Initial molarity of KI stock, 0.04072; normality of $KIO_3$, 0.005712

| *n*-BuBr, g. | $(KI)_0$ ml.$^{-1}$ | *t*, hours | $(KI)_t$, ml.$^{-1}$ | % reacted | *k* l.m.$^{-1}$ hr.$^{-1}$ |
|---|---|---|---|---|---|
| | 1. *n*-Butyl bromide at 15° | | | | |
| 0.1417 | 0.03984 | 0.860 | 0.02963 | 25.5 | 0.754 |
| .1462 | .03981 | 1.285 | .02562 | 35.6 | .743 |
| .1431 | .03983 | 2.909 | .01503 | 62.2 | .767 |
| .1422 | .03984 | 2.903 | .01500 | 62.3 | .775 |
| .1329 | .03990 | 3.778 | .01263 | 68.2 | .763 |
| .1415 | .03984 | 3.967 | .01104 | 72.2 | .763 |
| | | | | Av. | 0.761 |
| Ether, g. | | | | | |
| | 2. β-Bromoethyl-*n*-butyl ether at 25° | | | | |
| 0.1843 | 0.03956 | 3.037 | 0.02898 | 26.7 | 0.232 |
| .1799 | .03958 | 4.722 | .02508 | 36.5 | .226 |
| .1801 | .03958 | 7.813 | .01866 | 53.7 | .228 |
| .1853 | .03956 | 9.425 | .10594 | 59.8 | .226 |
| .1871 | .03949[a] | 10.378 | .01449 | 63.4 | .226 |
| .1878 | .03955 | 11.483 | .01272 | 67.8 | .232 |
| | | | | Av. | 0.228 |

[a] Initial molarity of KI stock, 0.04065.

TABLE III

| RX | $(RX)_0$ | $(KI)_0$ | Temp., °C. | *k* |
|---|---|---|---|---|
| $C_2H_5OCH_2CH_2Br$ | 0.1945 | 0.03961 | 25° | 0.251 ± 0.026[a] |
| $C_2H_5OCH_2CH_2Cl$ | .2962 | .01934 | 35° | $1.54 \times 10^{-3}$ |

[a] Corrected for iodine liberation.

To study possible coprecipitation of potassium iodide and reversibility of the reaction a solution was made up in which the *n*-butyl bromide was 0.09888 *M* and the potassium iodide was 0.04041 *M*, and allowed to stand at 25° until no more reaction occurred, whereupon two samples were withdrawn and titrated. The iodide ion concentration was found to be 0.001409 *M*, representing apparently 96.5% reaction. The supernatant liquid was removed and the solid washed several times with acetone, then titrated for iodide ion. The amount found indicated that the reaction had gone 95.9% to completion. A calculation of an approximate equilibrium constant based on these data similar to a reported calculation for the analogous methyl bromide reaction[19] gave 0.59. Other measurements of an approximate equilibrium constant using the 10-ml. flask technique, with the concentrations used in the kinetic runs, invariably showed the reverse specific reaction rate to be greater than the forward one, but were erratic (0.19–0.37). Rough estimates of coprecipitation were made in some individual sample runs too. At the time the reaction was to be quenched the supernatant liquid was poured into the acid mixture, the solid rinsed with acetone, the rinsings added to the beaker, and the contents titrated. The solid was dissolved and titrated separately. These results indicated some, but not excessive, coprecipitation. The reversibility effect would tend to lower the rate constants slightly at the higher percentages of reaction.

Consistent rate constants were obtained by following a regular system of shaking the flasks for each run. When there was little shaking or none, the calculated rate constants were lowered slightly. Coprecipitation of potassium iodide causes more iodide ion to be removed from the solution than there should be from merely the reaction with the organic bromide. However, when the individual sample technique is employed an exact percentage reaction is obtained.

Table IV presents the results of the rate measurements and the calculations of Arrhenius activation energies from the equation

$$k = Ae^{-E/RT}$$

where *E* is in kcal. per mole.

TABLE IV

RESULTS OF RATE MEASUREMENTS

| Compound | *n*-BuBr | *n*-$BuOCH_2CH_2Br$ | $MeOCH_2CH_2Br$ |
|---|---|---|---|
| $k_{15°}$ | 0.761 | 0.0751 | 0.0855 |
| $k_{25°}$ | 2.04 | .228 | 0.262 |
| $k_{35°}$ | 4.97 | .597 | |
| $E_{15-25°}$ | 16.8 | 18.9 | 19.1 |
| $E_{25-35°}$ | 16.3 | 17.6 | |
| $E_{av}$ | 16.55 | 18.25 | |

The specific reaction rate of β-chloroethyl ethyl ether relative to *n*-butyl chloride at 35° can be calculated using Conant and Hussey's activation energy of 19.6 kcal.[20] for the latter compound, obtained from measurements at 50 and 60°. It is 0.158, in general agreement with the values for the bromo compounds studied here. Kirner found, at 50°, the relative reactivity of β-chloroethyl phenyl ether to be 0.308. When his activation energy for the ether is used, with 19.6 kcal. for *n*-butyl chloride, the ratio becomes 0.248 at 35°, which indicates that the alkyl ether is less reactive in this case. Kirner thought that the activation energy for *n*-butyl chloride was 22.5 kcal.,[6] while those for his β-chloroethers he found to be 21.6–22.9 kcal. If the value of 19.6 kcal. he accepted for *n*-butyl chloride, then the decreased reactivity that Kirner found would appear to be cause by an increased *E*, in concordance with the results given in this paper.

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(19) E. A. Moelwyn-Hughes, *Trans. Faraday Soc.*, **45**, 167 (1949).

(20) J. B. Conant and R. E. Hussey, THIS JOURNAL, **47**, 476 (1925).