necessary to measure the reaction rates in dilute solutions; this would be very difficult to do experimentally.

The general problem of uniquely determining the rate-determining step in general acid catalyzed reactions has been much discussed, and only in a few reactions has it been possible to settle the problem experimentally, for example, in the case of the enolization of acetone. However, from the data in the oxygen exchange reaction between acetone and water, it can be concluded that the rate of ionization of acetone as a base is not slower than the rate of oxygen exchange.

It would be of some interest to measure the rate of exchange of oxygen between acetone and water in D_2O. The experimental work of Reitz[15] on the enolization of both light and heavy acetone in both light and heavy water gives the change in the equilibrium constant of the ionization of acetone in light and heavy water. If the oxygen exchange reaction involves the same equilibrium, this would tend to increase the rate of reaction in D_2O. On the other hand, if equilibrium were not attained in the first step, and the rate of ionization were rate determining, there would be a decided decrease in the rate of D_2O.

We are indebted to Dr. Marvin Fox for the analyses of many of our samples, and also to Prof. L. P. Hammett for many valuable discussions and suggestions in regard to this work.

Summary

1. The existence and the approximate rates of exchange for reactions between oxygen in water in some typical organic compounds have been investigated, with the use of waters ranging from 0.080 to 0.750% O^{18}.

2. It was found that the oxygen of hydroxyl and carboxyl groups (except chloroacetic acids) does not exchange with water, but the oxygen of the carboxyl group in both acetone and acid aldehyde does exchange with water, the latter more rapidly than the former.

3. A detailed kinetic study of the reaction between acetone and water revealed that the reaction was catalyzed by hydrogen ions, by hydroxyl ions, and by salicylic acid molecules, but not by salicylate ions.

4. The catalytic coefficients of the hydrogen ion and salicylic acid molecule for a bimolecular reaction between water and acteone in a 10% water–90% acetone medium were 116.5 and 0.0683 (m./l.)$^{-1}$ min.$^{-1}$, respectively.

5. The difference between these rates and the rates of the enolization of acetone shows that the exchange of the oxygen does not proceed through the enolic form although it has been shown that the exchange with hydrogen does. The rate of ionization of acetone as a base cannot be slower than the rate of oxygen interchange.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

The Oxidation of Iodide Ion by Persulfate Ion. V. The Rate at Low Ionic Strength

BY ORAN M. KNUDSEN AND CECIL V. KING

Measurements of the rate of the persulfate-iodide ion reaction in aqueous solutions of low ionic strength reported in paper IV of this series[1] indicated the primary salt effect to be in good agreement with the predictions of the Brönsted theory.[2] These earlier measurements were made by adding small, known amounts of thiosulfate to the reaction mixtures and noting the time of appearance of iodine photoelectrically, without the aid of starch or other indicator.

New measurements of the rate were published in 1933 by Soper and Williams,[3] with significantly different results. While at the ionic strength 0.025 some of their results agreed well with those of other workers, as will be discussed later, their values at lower ionic strengths fell off in such a way that the slope of the log k *vs.* $\sqrt{\mu}$ curve became about 2.5 rather than the theoretical 2.0 to 2.08 at 25°.

Soper and Williams made up their solutions in 500- or 1000-cc. flasks, withdrew samples from time to time and titrated with 0.002 N thiosulfate while bubbling nitrogen through the solution to exclude oxygen.[4] While exact details are not given, no mention is made of any unusual precautions in titrating the exceptionally dilute

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[1] King and Jacobs, THIS JOURNAL, **53**, 1704 (1931).

[2] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

[3] Soper and Williams, *Proc. Roy. Soc.* (London), **A140**, 59 (1933).

[4] Soper, *J. Chem. Soc.*, **125**, 1899 (1924).

iodine solutions involved, except those designed to ensure a sharp end-point.

It is well known that an appreciable amount of iodine must be present to give a visible color with starch, that this amount varies with the concentration of iodide and of other salts, and that corrections must be applied in titrating solutions of iodine less than about 10^{-4} molar. Kolthoff[5] has suggested a (rather unsatisfactory) method of applying such corrections. Woodard[6] has described a colorimetric procedure in which correction factors are applied for iodine solutions below 2×10^{-4} molar. Müller and McKenna[7] have studied the iodine–starch–iodide system in some detail from a colorimetric standpoint. They show that in a solution containing 2×10^{-4} molar iodide, almost 1×10^{-5} molar iodine must be present to cause any noticeable light absorption. Theoretically, if twice this iodine concentration were present, little more than half would be revealed by thiosulfate titration. In practice, we find the correction to be somewhat smaller, probably because of a tendency to pass the end-point in titration, with atmospheric oxygen present.

If Soper's work with Williams and others were to be taken seriously, a complete reëxamination of the theoretical behavior of dilute solutions of electrolytes would be necessary. The present investigation was undertaken to establish the feasibility of determining iodine accurately in the dilute solutions necessary, by the application of empirical correction factors, and finally to apply the method to persulfate–iodide rate experiments. Consequently empirical "calibration curves" were first established for the titration with thiosulfate, over the range of iodine, potassium iodide and potassium nitrate concentrations used in the rate experiments. For the most dilute solutions the correction amounts to nearly 100%.

Reagents.—Most of the *water* used was redistilled from acid permanganate with a quartz still and condenser. *Sodium thiosulfate* was recrystallized and dried in air. Sterile stock solutions (about 0.05 molar) were standardized by the neutral solution–persulfate–iodide method.[8] Their titer remained constant for at least one month. Solutions about 0.002 molar were made by quantitative dilution on the day they were to be used.

Potassium iodide was recrystallized from water and then from alcohol to free it from traces of iodine. Standard solutions were made by direct weighing. *Potassium nitrate* was recrystallized from water and solutions made by weighing. *Potassium persulfate* was freed from sulfate by recrystallizing between 50 and 0°. Solutions were made by weighing immediately before use. Soluble *starch* was used, fresh 1% solutions being made frequently. Two cc. was used for each titration.

Calibration of the Iodine Titration.—To establish the calibration curves, saturated or nearly saturated solutions of iodine in pure water were made and standardized against the stock thiosulfate (0.05 M), a suitable amount of potassium iodide being added to each sample during the titration. The thiosulfate solution was then diluted quantitatively to about 0.002 molar, the iodine to a suitable concentration between 5×10^{-6} and 7×10^{-5} molar, with addition of potassium iodide and nitrate as shown below. Portions of 150 cc. of iodine solution were then placed in 200-cc. round-bottomed flasks and titrated, using a white porcelain cup as background and suitable illumination, with thiosulfate from a 10-cc. semimicro buret. After some practice the titration could be repeated with a maximum divergence of 0.06 cc. No attempt was made to eliminate oxygen for fear of expelling iodine.

Forty to sixty samples were titrated for each iodide and nitrate concentration. Several methods could be used for applying the results obtained. It was found convenient to plot the logarithm of the ratio (True iodine concentration)/(Apparent iodine concentration) = log $(C^0_{I_2}/C'_{I_2})$ *vs.* the logarithm of the apparent iodine concentration (= log C'_{I_2}); a smooth curve was drawn as well as possible through these points, and when

TABLE I

TITRATION OF IODINE SOLUTIONS WITH THIOSULFATE

$C^0_{I_2}$, $M \times 10^6$		6	10	20	30	40	50	70
C_{KI}, M	C_{KNO_3}, M	$C'_{I_2} \times 10^6$ Apparent iodine concentration						
0.00025	......	2.1	5.2	13.8	22.7	32.3	42.1	61.5
.00080	......	3.0	6.0	14.2	23.9	34.3	45.8	..
.001025	......	3.0	6.0	14.2	23.4	33.2	43.5	..
.001625	......	3.1	6.5	15.7	25.2	34.9	44.7	64.4
.006025	......	3.4	7.8	18.2	28.8	39.1	..	..
.010	......	4.0	8.3	19.0	29.5	39.8	50	..
.0235	......	4.0	8.3	19.0	29.8	40.0	..	..
.00025	0.005775	2.7	5.9	14.9	24.0	33.9	44.0	64
.001025	.001375	2.9	6.0	14.9	24.0	33.3	43.5	65
.0025	.000775	2.8	5.7	14.1	23.0	32.2	42.0	62.8
.006025	.0175	4.0	7.8	17.2	26.9	36.8	47.0	68.0

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(5) Kolthoff and Furman, "Volumetric Analysis," John Wiley and Sons, Inc., New York, N. Y., Vol. II, 1929, p. 350.

(6) Woodard, *Ind. Eng. Chem., Anal. Ed.*, **6**, 331 (1934).

(7) Müller and McKenna, THIS JOURNAL, **58**, 1017 (1936).

(8) King and Jette, *ibid.*, **52**, 608 (1930). Earlier references are given.

the rate measurements were made a correction could be applied easily to each titration from the most suitable curve. One such curve is shown in Fig. 1 and the results of all such calibration titrations are given for round concentrations of iodine in Table I.[9]

There are some discrepancies in the values obtained in this way, as the figures of Table I indicate. For instance, some of the values for 0.001025 *M* potassium iodide are lower than those for 0.0008 *M* iodide, though they evidently should be higher. The maximum deviation of individual points from the smoothed values were as follows: at $C^0_{I_2} = 6 \times 10^{-6}\ M$, ±14%; at $10 \times 10^{-6}\ M$, ±4%; at $15 \times 10^{-6}\ M$, ±3%; and at higher concentrations, ±2%.

Persulfate could not, of course, be added to the solutions in these calibration titrations. Other inert salts of the same valence type could have been added, but it is doubtful whether concentrations as low as those used in the rate experiments would change the correction factors appreciably. It should be noted that the iodide concentration at the end of the titration is higher than that added initially by the amount $2 \times C'_{I_2}$.

Rate Measurements.—When the rate was slow enough to warrant it, 150-cc. portions of the initial solutions were sealed in 200-cc. flasks and immersed in the thermostat (at 25 ± 0.02°). At suitable time intervals two or more flasks were opened and the contents titrated. In the faster experiments the solutions were kept in glass-stoppered flasks. Rate "constants" were calculated from one of the integrated forms of the bimolecular equation

$$-dC_{S_2O_8^=}/dt = kC_{S_2O_8^=}\,C_{I^-}$$

where the *C*'s are concentrations in moles per liter and *t* the time in minutes. Because of triiodide formation and perhaps other reasons the value of *k* decreases with time and to obtain comparable measures of the rate an extrapolation to zero time must be made.

Table II shows the details of a typical rate experiment at nearly the lowest ionic strength used.

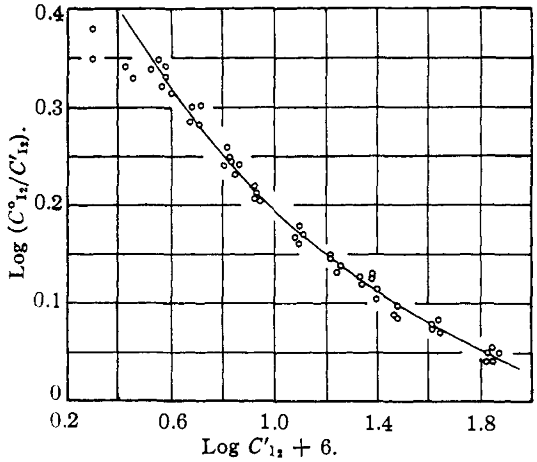

Fig. 1.—Logarithmic "calibration curve" for the iodine titration with 0.00025 *M* potassium iodide present initially.

In this and other slow experiments two to four titrations were made within a few minutes and the results averaged; in faster experiments values of *k* were calculated from each titration. In the experiment of Table II the ratio $C^0_{I_2}/C'_{I_2}$ was interpolated from the logarithmic curves for 0.00025 molar and 0.0008 molar iodide. In other cases the appropriate curve was used or interpolation between two curves made. The values of *k'* are bimolecular "constants" calculated from the apparent iodine concentrations.

TABLE II

DETAILS OF A TYPICAL RATE EXPERIMENT

Initial concentrations: $C_{K_2S_2O_8} = 0.000114\ M$, $C_{KI} = 0.000455\ M$.

Time, min.	Thiosulfate,[a] cc.			C'_{I_2}, *M* $\times 10^6$	$C^0_{I_2}$, *M* $\times 10^6$	*k'*	*k*
0	..	..	..	..	..	....	(0.095)
3100	1.13	1.09	1.17	7.35 av.	12.6	0.0485	.0859
7125	2.20	2.23	2.34	14.7	21.1	.0443	.0673
10200	3.05	3.16	3.12	20.2	27.3	.0443	.0632
15000	4.15	4.18	4.09	26.9	34.3	.0420	.0573

[a] 0.00195 *M*, to titrate 150-cc. samples.

Figure 2 shows the extrapolation of *k* to zero time for three typical experiments. While these linear extrapolations are not very satisfactory for a number of reasons, probably no more error is involved than in other parts of the procedure. The points at lowest time and iodine concentration are seen to be very important, since if they were neglected the extrapolated values would as a rule be several per cent. lower. If sufficient data were obtained for each experiment, the extrapolation to zero time presumably could be avoided by the method used in paper I of this series.[10] Actually,

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[9] It has been suggested by Professor William C. Bray (privately) that a portion of the discrepancy between the true and apparent iodine concentrations may be due to some oxidation of thiosulfate to sulfate rather than tetrathionate in these very nearly neutral solutions of low iodide content (*cf.* Bray and Miller, THIS JOURNAL, **46**, 2204 (1924)). This may well be true, and in preliminary experiments an attempt was made to avoid this possibility by adding a drop or two of dilute sulfuric acid during the titration. However, this made it impossible to obtain satisfactory end-points, presumably due to more rapid oxygen absorption; rather than attempt to exclude oxygen, it was decided to assume that errors in the calibration, whatever their source, counterbalanced similar errors in the titrations of the rate experiments.

[10] Jette and King, THIS JOURNAL, **51**, 1034 (1929).

in the very slow experiments the rates seem to decrease too much with time to be accounted for entirely by triiodide formation. There may be some oxidation of iodine to iodate in these solutions.

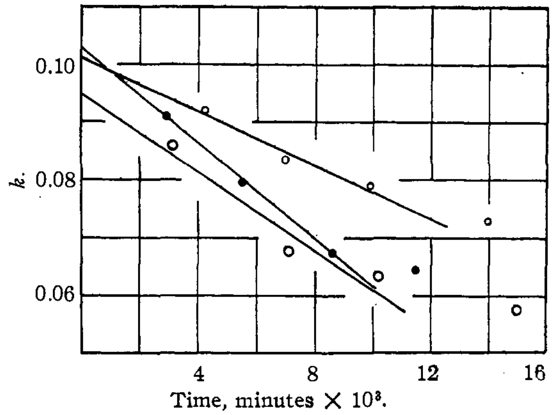

Fig. 2.—Extrapolation of rate "constant" to zero time: large circles, Expt. 5 (Table III); small circles, Expt. 8; black circles, Expt. 6.

Table III summarizes all the rate experiments. In Fig. 3 values of log k are plotted *vs.* $\sqrt{\mu}$, the square root of the ionic strength. Four points of Table III are omitted because of obviously gross errors. The theoretical limiting relation is, at 25°

$$\log k = \log k_0 + 2\sqrt{\mu}$$

where k_0 is the value of k extrapolated to $\sqrt{\mu} = 0$. The straight line of Fig. 3 is drawn with the slope 2. Its equation is

$$\log k = -1.07 + 2\sqrt{\mu}$$

giving $k_0 = 0.0852$. The relation is satisfactory as a limiting one, and divergence at higher ionic strengths is in the direction to be expected theoretically. The agreement with the work of King and Jacobs is also excellent; these authors found, for solutions containing mostly uni-univalent salts, the limiting relation

$$\log k = -1.075 + 2\sqrt{\mu}$$

and $k_0 = 0.0841$.

TABLE III

EFFECT OF IONIC STRENGTH ON THE RATE OF THE PERSULFATE–IODIDE REACTION AT 25°

Expt.	$C_{K_2S_2O_8}$, M × 10^4	C_{KI}, M × 10^4	C_{KNO_3}, M × 10^4	$\sqrt{\mu}$	k
1	1.17	2.34	....	0.0242	0.104
2	1.25	2.50	....	.0250	.101
3	1.25	2.50	....	.0250	.089
4	1.25	2.50	....	.0250	.084
5	1.14	4.55	....	.0280	.095
6	2.00	4.00	....	.0315	.103
7	1.10	2.20	6.84	.0351	.098
8	1.25	2.50	7.75	.0374	.101
9	1.25	10.25	....	0.0374	0.108
10	1.25	2.50	7.75	.0374	.104
11	2.00	8.00	....	.0374	.102
12	1.25	2.50	14.20	.0452	.100
13	1.25	16.25	....	.0452	.105
14	1.25	2.50	13.75	.0452	.109
15	7.97	24.16	....	.0693	.116
16	7.97	24.16	....	.0693	.116
17	1.25	2.50	57.75	.0800	.122
18	1.25	60.25	....	.0800	.124
19	1.25	60.25	....	.0800	.098
20	18.0	16.0	....	.0836	.123
21	18.0	16.0	....	.0836	.122
22	3.00	6.00	85.0	.100	.130
23	3.00	6.00	85.0	.100	.129
24	3.00	100.0	....	.104	.116
25	5.00	100.0	....	.107	.120
26	5.00	100.0	....	.107	.133
27	5.00	100.0	....	.107	.139
28	2.50	110.0	....	.108	.131
29	5.00	100.0	135.0	.158	.128
30	5.00	235.0	....	.158	.161
31	5.00	235.0	....	.158	.167
32	5.00	235.0	....	.158	.163
33	5.00	60.25	175.0	.158	.171
34	5.00	60.25	175.0	.158	.171
35	5.00	60.25	175.0	.158	.173
36	10.0	235.0	....	.1630	.163
37	10.0	235.0	....	.1630	.165
38	10.0	60.25	175.0	.1630	.171
39	10.0	60.25	175.0	.1630	.169

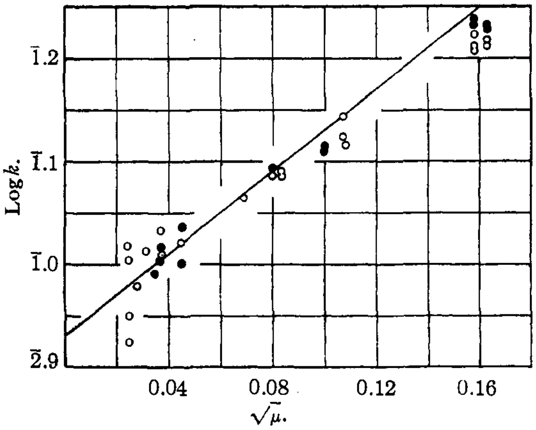

Fig. 3.—The plot of log k *vs.* $\sqrt{\mu}$: black circles, potassium nitrate present.

Discussion

It is obvious that the titration method used here, though not to be recommended for the accurate determination of iodine in dilute solution, is sufficiently accurate for the purpose at hand. Personal and other errors made in the calibration titrations closely balance, on the average, similar errors made in the titrations in the rate experiments. Maximum deviations of k from the mean are, at the lowest ionic strengths, ±12%; at higher ionic strengths, ±4 to 5%. While these errors are higher than desirable, the trend of the results is not obscured.

Extrapolated values of k' the rate "constant" calculated directly from the titrations with no correction, agree well with the values of Soper and Williams. Table IV compares at round values of $\sqrt{\mu}$, k(Soper and Williams), k', k(present investigation) and k(King and Jacobs), all for low persulfate concentration and added uni-univalent salts to make up the ionic strength.

TABLE IV

COMPARISON OF RATE CONSTANTS

$\sqrt{\mu}$	k^a	k'	k^b	k^c
0.03	0.062	0.063	0.098	0.097
.05	.066	.068	.107	.106
.08	.081	.080	.123	.122
.10	.092	.096	.133	.131
.16	.123	.125	.168	.166

[a] Soper and Williams. [b] Knudsen and King. [c] King and Jacobs.

Before an investigation can be made of such "medium effects" as those postulated by Soper and Williams, it is evident that there must be a clear understanding of the normal salt effects. For example, for solutions containing 0.005 molar persulfate, 0.01 molar iodide, Soper and Williams found $k = 0.123$, in excellent agreement with the value 0.125 found by Jette and King,[10] who investigated the rate in this particular solution very thoroughly. Here the iodine rapidly attains such a concentration that no correction need be applied to the titration. For approximately the same solution King and Jacobs found $k = 0.133$ and explained the discrepancy to some direct oxidation of thiosulfate by persulfate. For a second solution of the same ionic strength (0.025) but containing 0.0002 molar persulfate and 0.0244 molar iodide, Soper and Williams found $k = 0.122$. The salt effect in this second solution should evidently be much higher than in the first because most of the ions are univalent. For similar solutions the present investigation gives $k = 0.167$ while King and Jacobs found practically the same. Soper and Williams are in error because the iodine is liberated very slowly in the second solution and large corrections are necessary in all the titrations.

Summary

The titration of iodine with thiosulfate has been investigated in solutions 5×10^{-6} to 7×10^{-5} molar, using starch as the indicator, and empirical "calibration curves" have been established for various concentrations of potassium iodide and nitrate.

The rate of the persulfate–iodide ion reaction has been investigated between the ionic strengths 0.0006 and 0.025, by titrating the iodine formed and applying corrections as indicated by the "calibration curves."

The primary salt effect is found to be in agreement with the predictions of the Brönsted theory. The rate measurements are in excellent agreement with those found previously in this Laboratory by a different experimental method.

NEW YORK, N. Y. RECEIVED JANUARY 6, 1938

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

A Mass Spectrographic Determination of the Isotope Abundance and of the Atomic Weight of Rubidium

BY A. KEITH BREWER

Rubidium is one of the most widely distributed of all the elements and yet there are no ores in which it is concentrated more than a few per cent. It is of particular interest in that it is the most radioactive of all the elements outside of the so-called "radioactive elements." The radioactivity consists of a soft beta ray, with no detectable alpha or gamma emission.

The present paper presents (1) a measurement of the abundance ratio of the isotopes of rubidium in various natural sources, (2) a mass spectrographic determination of the atomic weight from these ratios, (3) a study of the disintegration products of the radioactive isotope, and (4) a discussion of the effect of the radioactivity of rubidium on the atomic weight of strontium.

I. The Rb^{85}/Rb^{87} Ratio

Aston[1] assigns $Rb^{85}/Rb^{87} = 3.0$ as the most probable value. Bondy, Johannsen and Popper[2] using rubidium carbonate as a source obtained a

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(1) Aston, "Mass Spectra and Isotopes," 1933.

(2) Bondy, Johannsen and Popper, *Z. Physik*, 95, 46 (1935).