In the standard procedure,[15] 10 ml. of toluene is pipetted into a dry 250-ml. flask which can be fitted to either a reflux condenser or a distillation condenser by an interchangeable ground glass joint. Exactly 1 ml. of acetyl chloride is added by means of a calibrated pipet. The selected amount of catalyst (powdered, if solid) is then added all at once, suitable precautions having been taken to minimize hydrolysis during its measurement. Timing is begun from the first visible sign of reaction, usually bubbling; this may or may not require preliminary heating. During the reaction a further 5 ml. of toluene is dripped down through a loose plug of glass wool midway in the reflux condenser, to scrub acetyl chloride vapor from the escaping hydrogen chloride. As soon as any vigorous reaction subsides the flask is heated in boiling water and in some cases with a free flame afterward; for estimating reaction times, the time of refluxing over a flame (at about 110°) is doubled and added to time of heating in the water-bath.

After whatever time of reaction chosen is complete, the flask is quickly cooled and its contents hydrolyzed by adding cold water through the condenser. The reaction mixture is made just alkaline to phenolphthalein, diluted to about 150 ml., and distilled into a separatory funnel until at least 75 ml. of distillate have been collected, the last droplets of ketone being swept out of the condenser with steam. Plugs of glass wool in the neck of the flask are used to prevent spray from being carried over.

Fifteen grams of sodium nitrate is dissolved in the distillate by shaking, for its salting-out effect. The toluene layer is then separated and the salt solution and containers are washed with two 5-ml. portions of benzene to rinse out all ketone. The accumulated solution containing the *p*-methylacetophenone is treated with 20 ml. of an approximately 0.5 *N* neutral solution of hydroxylamine hydrochloride in methanol, and allowed to stand overnight. The liberated hydrochloric acid is then titrated with a standard solution of sodium methoxide in methanol, using butter yellow as indicator. The titration is renewed at any convenient intervals, usually about twenty-four hours, until a permanent end-point is reached. This stepwise titration should be accompanied by a blank, and indeed the whole process of isolating and determining the ketone should be tested with known amounts. By such a test we can recover 99% of samples of acetophenone or *p*-methylacetophenone. Blanks may also be run through the whole procedure, omitting only the acetyl chloride, when there is any suspicion that a catalyst is somehow producing spurious evidence of yield, perhaps by catalytic decomposition of hydroxylamine.

## Summary

1. Thirty-nine anhydrous metallic chlorides have been tested as catalysts for the Friedel–Crafts synthesis of *p*-methylacetophenone from acetyl chloride and toluene. Of these, twenty-eight showed no catalytic power at the boiling point of toluene. A comparison of most of the others, at optimum concentration and reaction time for each, yields the following order of decreasing efficiency: $AlCl_3$, $SbCl_5$, $FeCl_3$, $TeCl_2$, $SnCl_4$, $TiCl_4$, $TeCl_4$, $BiCl_3$, $ZnCl_2$. Of these, bismuth trichloride and tellurium dichloride have not previously been reported as catalysts.

2. Several of the catalysts produce a rapid decrease in yield as the reaction time is increased, doubtless because they catalyze auto-condensation of the product.

3. Several of the catalysts, notably titanium tetrachloride, give maximum yields at catalyst/acid chloride ratios several times greater than the 1:1 value often recommended.

STILLWATER, OKLAHOMA RECEIVED MAY 9, 1941

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[15] Used for all catalysts except antimony pentachloride, which was tested by use of the Perrier procedure [*Ber.*, **33**, 815 (1900)].

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[CONTRIBUTION FROM THE CHARLES E. COATES CHEMICAL LABORATORIES, LOUISIANA STATE UNIVERSITY]

# Dielectric and Solvent Effects upon the Iodide–Persulfate Reaction

BY EDWARD S. AMIS AND JAMES E. POTTS, JR.

Amis and co-workers[1–3] have begun an extensive investigation of ion-ion and ion-dipole reactions in various mixed solvents of controlled dielectric constant, in order to inquire into the electrostatic effects of the solvent and also the specific solvent effects upon a given reaction.

The alteration of the coulombic energy of activation for a reaction with a change in the dielectric constant of the solvent may be calculated from the equation[1]

$$\Delta E_e^* = \frac{-Z_1Z_2e^2}{D_1D_2r}\Delta D \qquad (1)$$

Also, the differences in energies of activation for a reaction when measured in media of constant composition and isodielectric media may be calculated by the equation derived by Amis and Holmes.[3] This equation may be written

$$\Delta E_C^{*'} - \Delta E_D^{*'} = \frac{Z_1Z_2e^2NT}{D^2J}\left(\frac{1}{r} - \frac{3e}{10}\sqrt{\frac{2\pi N\mu}{10DkT}}\right)\frac{\mathrm{d}D}{\mathrm{d}T} \qquad (2)$$

By combining these equations the authors have obtained the expression

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[1] E. S. Amis, THIS JOURNAL, **63**, 1606 (1941).

[2] E. S. Amis and S. E. Cook, *ibid.*, **63**, 2621 (1941).

[3] E. S. Amis and F. C. Holmes, *ibid.*, **63**, 2231 (1941).

$$\Delta E_C^* - \Delta E_D^* = \frac{Z_1Z_2e^2N}{D_CJ}\left[\left(\frac{1}{r} - \frac{3e}{10}\sqrt{\frac{2\pi N\mu}{10D_CkT}}\right)\frac{T\mathrm{d}D}{D_C\mathrm{d}T} - \frac{\Delta D}{D_Dr}\right] \quad (3)$$

for calculating the difference in energies of activation for a constant composition run of a given dielectric constant and for an isodielectric run of any dielectric constant. In this equation $\Delta D = D_C - D_D$, where $D_C$ and $D_D$ are the dielectric constants of the isocomposition and of the isodielectric runs, respectively. When c. g. s. — e. s. u. units are used for the other quantities and the mechanical equivalent of heat, $J$, is in ergs per calorie then $\Delta E_C^* - \Delta E_D^*$ is in calories. The advantage of this equation is obvious since one accomplishes by one calculation that which was formerly obtained only by two separate calculations.

In order to test further electrostatic and specific solvent effects upon reaction rates and to obtain data to substantiate equation (3), the authors studied the persulfate–iodide reaction in isocomposition and isodielectric water–ethyl alcohol mixtures. The accepted mechanism for this reaction is as follows[4–6]

$S_2O_8^{--} + I^- \longrightarrow (S_2O_8I)^{---}$ (Measurable)
$(S_2O_8I)^{---} + I^- \longrightarrow 2SO_4^{--} + I_2$ (Instantaneous)

**Materials.**—Potassium persulfate (C. P. Merck) was purified by the procedure given by Jette and King.[6] When dissolved in water it gave no detectable test for sulfate ions. Ordinary distilled water was found to exhibit a pronounced catalytic effect and it was necessary therefore to redistil it through an all-Pyrex glass still with added acid permanganate. Anhydrous alcohol was prepared by the procedure of G. F. Smith.[7] The potassium iodide and nitrate and the sodium thiosulfate were recrystallized at least twice from distilled water. The first was also recrystallized from alcohol and freshly prepared solutions showed no free iodine for twenty-four hours. The thiosulfate solutions were made up from freshly boiled water and chloroform was added as a preservative. The solutions were stored in opaque bottles and showed no change in concentration when analyzed by the method of King and Jette.[8] Temperatures were measured to within 0.02° on a calibrated thermometer.

The procedure used in making a run was as follows. Equivalent quantities of the two reactants, potassium persulfate and potassium iodide, were weighed out to four decimal places and diluted to the correct volume at the temperature at which the run was to take place. The alcohol–water mixtures were also made up by weight, using the tables of Akerlof.[9] One-hundred-milliliter portions of potassium persulfate solution were pipetted out of the stock solution into a ground-glass-stoppered reaction flask which was then placed in the water-bath. When temperature equilibrium had been reached, an equal volume of the potassium iodide solution was pipetted into the reaction flask, after which the flask was thoroughly shaken to ensure uniform mixing. The time $t_0$ was taken at the instant the last drop of the iodide solution fell. The time intervals were measured with a fifth-second stop watch. After a given time, a 25-ml. portion was pipetted out and titrated rapidly with the standard thiosulfate solution, using starch indicator. The volume of the thiosulfate used was measured from a 10-ml. calibrated Machlett Auto Burette, which could be read to within 0.01 ml. The procedure in making the salt effect runs was identical with the above except that the required weight of potassium nitrate was added to the solution of potassium persulfate in the reaction flask before the addition of the potassium iodide.

**Discussion of Data.**—In Table I are recorded the values of the reaction rate constant, the frequency factor $B$ of the Arrhenius equation and the energies of activation of the iodide–persulfate reaction in isocomposition and isodielectric media at various temperatures. The compositions and the dielectric constants of the various media are specified. The reaction rate constants were calculated on the basis of a second order reaction in which equivalent quantities of the reactants were present. The equation is

$$k = \frac{1}{t}\,\frac{x}{a(a - x)} \quad (4)$$

where $t$ is the time in minutes. The concentrations of both iodide and persulfate were 0.02 $N$ for all runs. The bimolecular rate constants were found to decrease linearly with time over a period sufficiently long to permit extrapolation to zero time. This was the method followed by Soper and Williams,[10] Jette and King,[6] and Knudsen and King[11] to eliminate the effect of tri-iodide formation and also the effect of increasing ionic strength during the course of the reaction. In Fig. 1 are given representative extrapolations of $k$ to zero time at three different temperatures. Each value of $k$ recorded in Table I is an average of at least two duplicate runs, the extrapolated $k$ values of which gave a maximum deviation from the mean of 1%. Our method of procedure and extrapolation was acceptable since for a concentration of persulfate of 0.005 $M$ and that of iodide of 0.01 $M$ Soper and Williams[10] obtained 0.123, Jette and King[6] 0.125 and the authors 0.129, respectively, for the extrapolated values of $k$ in water at 25°. Only the rate in water could be

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(4) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).
(5) Kiss and Zombory, *Rec. trav. chim.*, **46**, 225 (1927).
(6) Jette and King, THIS JOURNAL, **51**, 1034 (1929).
(7) G. F. Smith, *Ind. Eng. Chem.*, *Anal. Ed.*, **1**, 72 (1929).
(8) King and Jette, THIS JOURNAL, **52**, 608 (1930).
(9) Akerlof, *ibid.*, **54**, 4125 (1932).
(10) Soper and Williams, *Proc. Roy. Soc.* (London), **A140**, 59 (1933).
(11) Knudsen and King, THIS JOURNAL, **60**, 687 (1938).

TABLE I

EXPERIMENTAL DATA FOR WATER AND ETHYL ALCOHOL–WATER MIXTURES

CONSTANT COMPOSITION

| Temp., °C. | $H_2O$ $k$ | $D$ | 7.7% alcohol $k$ | $D$ | 15.4% alcohol $k$ | $D$ |
|---|---|---|---|---|---|---|
| 20 | 0.117 | 80.37 | 0.0758 | 76.00 | 0.0497 | 71.40 |
| 30 | .233 | 76.73 | .155 | 72.40 | .0997 | 68.00 |
| 40 | .453 | 73.12 | .301 | 69.00 | .204 | 65.00 |
| $B$(20–30) | 8.14 | | 8.36 | | 7.86 | |
| $B$(30–40) | 8.41 | | 8.22 | | 8.73 | |
| $\Delta E^*$(20–30) | 12,160 | | 12,630 | | 12,280 | |
| $\Delta E^*$(30–40) | 12,530 | | 12,510 | | 13,490 | |

ISODIELECTRIC

| Temp., °C. | $D = 73.12$ $k$ | wt. % alc. | $D = 69.00$ $k$ | wt. % alc. | $D = 60.00$ $k$ | wt. % alc. | $D = 55.00$ $k$ | wt. % alc. |
|---|---|---|---|---|---|---|---|---|
| 20 | 0.0603 | 12.5 | 0.0389 | 19.4 | .... | .. | .... | .. |
| 30 | .166 | 6.5 | .110 | 13.7 | 0.0510 | 29.3 | 0.0454 | 37.5 |
| 40 | .453 | 0.0 | .301 | 7.7 | .155 | 24.4 | .140 | 32.9 |
| $B$(20–30) | 12.11 | | 12.27 | | ... | | ... | |
| $B$(30–40) | 12.87 | | 12.72 | | 13.82 | | 13.97 | |
| $\Delta E^*$(20–30) | 17,870 | | 18,340 | | ... | | ... | |
| $\Delta E^*$(30–40) | 18,920 | | 18,970 | | 20,950 | | 21,220 | |

obtained at 50°, since alcohol reacted with the persulfate, as was indicated by the presence of aldehyde and the excessive disappearance of persulfate ions. At 40° a similar effect was noticeable in alcoholic solvents after five or six hours; however, the alcoholic persulfate solutions were used immediately after preparation and the reaction between persulfate and alcohol was insignificant during the time of the run.

In Table II are given the reaction velocity constants, the frequency terms and the energies of activation for various concentrations of potassium nitrate, the concentrations of iodide and persulfate being the same as in Table I. All these data were taken at a dielectric constant of 69.00 and for the temperature range indicated. The precision of the velocity constants in this table is of the same order as those recorded in Table I.

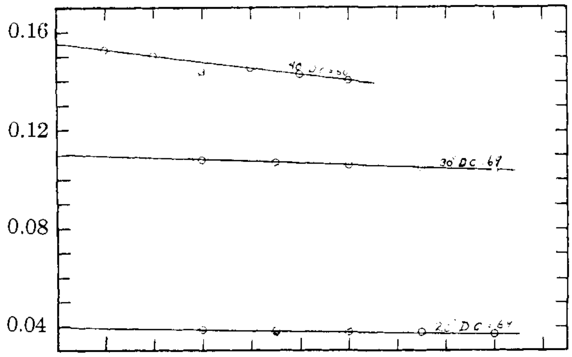

Fig. 1.

TABLE II

RATES, ENTROPIES OF ACTIVATION AND ENERGIES OF ACTIVATION FOR VARIOUS IONIC STRENGTHS IN ISODIELECTRIC MEDIA

$D = 69.00$

| $\sqrt{\mu}$ = | 0.212 | 0.235 | 0.308 | 0.380 |
|---|---|---|---|---|
| $k$(20°) | .0389 | .0485 | .0733 | .101 |
| $k$(30°) | .111 | .122 | .177 | .243 |
| $k$(40°) | .301 | .316 | .441 | .600 |
| $\Delta E^*_{20-30}$ | 18,340 | 16,270 | 15,560 | 15,490 |
| $\Delta E^*_{30-40}$ | 18,970 | 17,940 | 17,210 | 17,030 |
| $B_{20-30}$ | 12.29 | 10.81 | 10.57 | 10.58 |
| $B_{30-40}$ | 12.72 | 12.05 | 11.65 | 11.66 |

In Fig. 2 are plotted for isocomposition and isodielectric media the logarithms of the reaction rate constant *versus* the reciprocals of the absolute temperatures. Curves 1, 3 and 5 are for iso-

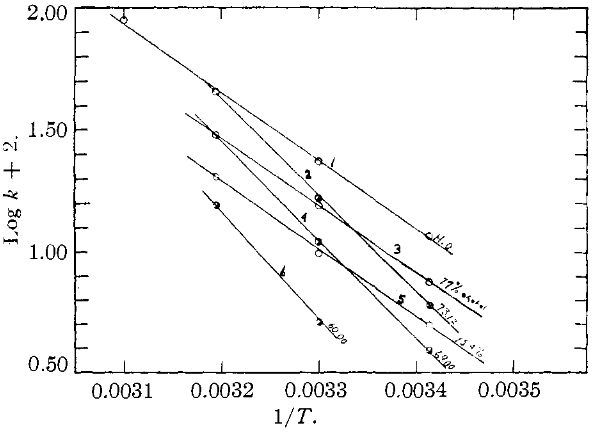

Fig. 2.—O, constant composition; ◑, constant dielectric constant.

composition media whose composition is specified. Curves 2, 4 and 6 are for isodielectric solvent mixtures, the dielectric constant being specified in each case. The difference in the slopes of the curves for the two kinds of media strikingly illustrates the variation of the temperature coefficient of the rates in the two cases.

In Fig. 3 are plotted the logarithms of the reaction velocity constants for the two kinds of solvent mixtures *versus* the reciprocals of the dielectric constants of these mixtures. The lines with negative slopes represent both isodielectric and isocomposition data while those with positive slopes are isocomposition lines. The fact that the log *k versus* $1/D$ lines break at lower dielectric constants is in agreement with the observations of LaMer,[12] and Amis and LaMer,[13] but in this case the break occurs at higher dielectric constants than was noticed by these authors. A possible explanation of this earlier break could be the difficulty of titrating to a definite starch–iodine end-point in solutions containing a high percentage of alcohol. The authors have observed that for solutoins containing as much as 30% alcohol, the starch end-point is not sharp.

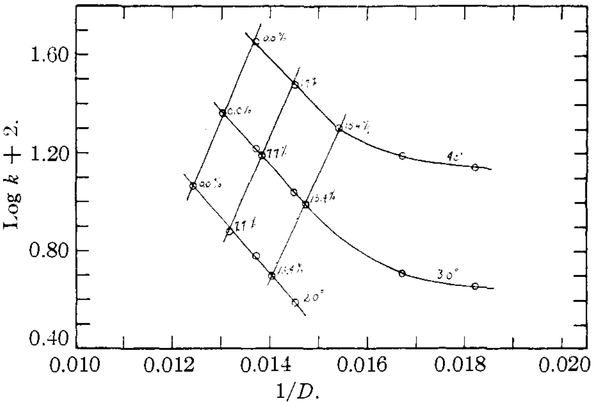

Fig. 3.

It is observable from Fig. 4, that the log *k versus* $\sqrt{\mu}$ plots approach the Debye–Hückel limiting law at these high concentrations. King and Jacobs[14] found for concentration increases of the reactants themselves agreement with the Debye–Hückel limiting law extended only to $\sqrt{\mu} = 0.06$. However, when the persulfate concentration was maintained at a low value and the ionic strength increased by adding either potassium iodide or potassium chloride the Debye–Hückel slope was obeyed to $\sqrt{\mu} = 0.16$, which is as high as their data extended. Knudsen and King,[11] using potassium nitrate to increase the ionic strength, obtained a like result. These facts do not necessarily lead to the conclusion that agreement between observation and theory would extend up to $\sqrt{\mu} = 0.212$, which is the point where our data begin, and, hence, the near agreement which we obtain may be due to the fact that our measured salt effect was observed in a mixed solvent of lower dielectric constant than that of pure water.

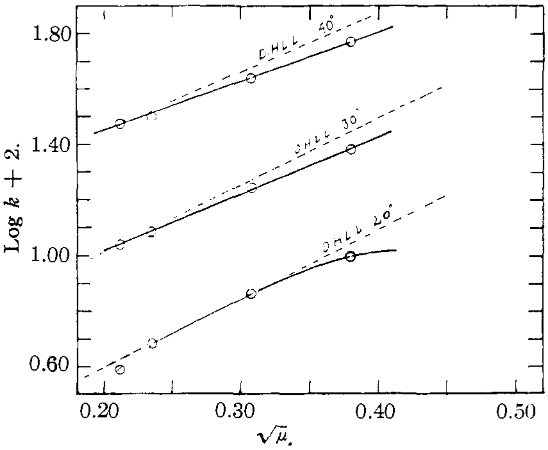

Fig. 4.

Kiss and Bossanyi,[15] using pure water as the solvent, observed a decreasing temperature coefficient with increasing temperature in the presence of neutral salts. Further, the temperature coefficient was found to be independent of the neutral salt concentration. From Table II, it is observable that when the reaction between iodide and persulfate is studied in mixed solvents of constant dielectric constant, an opposite trend of the critical increment with temperature is obtained. Also, the critical increment is definitely a function of the ionic strength, decreasing with increasing salt concentration. It can be seen also from Table II that the frequency factor in the Arrhenius equation increases with increasing temperature, and decreases with increasing ionic strength, when measurements of the salt effect are made in isodielectric media.

In Table III are collected the calculated values of $\Delta E_C^* - \Delta E_D^*$, using equation (3), together with the observed differences between these quantities. These calculations were made using the dielectric constants (indicated in column 1) of the isocomposition solvents corresponding to

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(12) LaMer, *J. Franklin Inst.*, **225**, 709 (1938).

(13) Amis and LaMer, THIS JOURNAL, **61**, 905 (1939).

(14) King and Jacobs, *ibid.*, **53**, 1704 (1931).

(15) Kiss and Bossanyi, *Rec. trav. chim.*, **47**, 619 (1928).

TABLE III

A COMPARISON OF OBSERVED AND CALCULATED DIFFERENCES IN ENERGIES OF ACTIVATION IN ISODIELECTRIC AND ISOCOMPOSITION WATER–ETHYL ALCOHOL MEDIA

| $D$ of isocomp. run | $D$ of isodiel. run | Obsd. $\Delta E_C^* - \Delta E_D$ | Calcd. $\Delta E_C - \Delta E_D$ |
|---|---|---|---|
| 78.54 | 73.12 | −5710 | −5850 |
| 78.54 | 69.00 | −6180 | −6440 |
| 74.15 | 73.12 | −5240 | −5690 |
| 74.15 | 69.00 | −5710 | −6240 |
| 69.70 | 73.12 | −5590 | −5470 |
| 69.70 | 69.00 | −6060 | −6070 |
| 74.87 | 73.12 | −6390 | −5820 |
| 74.87 | 69.00 | −6440 | −6420 |
| 74.87 | 60.00 | −8420 | −8010 |
| 74.87 | 55.00 | −8690 | −9120 |
| 70.70 | 73.12 | −6410 | −5670 |
| 70.70 | 69.00 | −6460 | −6270 |
| 70.70 | 60.00 | −8440 | −7860 |
| 70.70 | 55.00 | −8710 | −8970 |
| 66.40 | 73.12 | −5430 | −5450 |
| 66.40 | 69.00 | −5480 | −6050 |
| 66.40 | 60.00 | −7460 | −7640 |
| 66.40 | 55.00 | −7730 | −8750 |

the midpoint of the temperature range being studied, and for the dielectric constants (indicated in column 2) of the isodielectric solvents. The agreement between calculated and observed values is within the experimental error of the data. The larger variations at low dielectric constants of the solvent is not surprising since log $k$ is no longer a linear function of $1/D$ in this region.[12] The $r$ values used in calculating $\Delta E_C^* - \Delta E_D^*$ were 0.9 Å. The agreement of these calculated differences in the critical increments with observed differences in the two kinds of solvents shows that electrostatic forces are the predominant solvent effects upon the reaction.

Table IV contains observed and calculated values of $B_C - B_D$ using the equation[2]

$$B_C - B_D = \frac{Z_a Z_b e^2}{D^2 k}\left(\frac{1}{r} - \frac{3e}{10}\sqrt{\frac{2\pi N\mu}{10DkT}}\right)\frac{\mathrm{d}D}{\mathrm{d}T} \quad (5)$$

where $B_C$ and $B_D$ are the frequency factors for the isocomposition and isodielectric media, respectively. The $r$ values used in these calculations were the same as those for calculating $\Delta E_C^* - \Delta E_D^*$ in the two kinds of media. Again the precision obtained is within the limit of experimental error. In order to compare the $r$ values used in equations (3) and (5) with that obtained by the calculation based upon the plot of log $k_{\kappa=0}$ *versus* $1/D$, the authors, using the limiting form of the kinetic equation, calculated the values of log $k_{\kappa=0}$ at 30° from the data given in Table I for isocomposition solvents. These values were plotted against the respective $1/D$ values and from the slope of the straight line obtained, the value of $r$ in the Born term of the general kinetic equation was calculated. This method of calculation yielded a value of $r$ equal to 1.76 Å., which is nearly twice that used in the calculations of equations (3) and (5). LaMer[12] and also Laidler and Eyring[16] have given interesting discussions of this method for determining the radius of the Brönsted complex.

TABLE IV

A COMPARISON OF OBSERVED AND CALCULATED DIFFERENCES IN FREQUENCY FACTORS ($B$ VALUES) IN ISODIELECTRIC AND ISOCOMPOSITION ETHYL ALCOHOL–WATER MIXTURES

| Middle $D$ | $B$, const. comp. | $B$, const. dielect. | Obsd. $B_C - B_D$ | Calcd. $B_C - B_D$ |
|---|---|---|---|---|
| Temp. range 20–30°, mid. temp., °A. = 298.1 | | | | |
| 78.54 | 8.14 | 12.19 | −4.05 | −3.79 |
| 74.15 | 8.36 | 12.19 | −3.83 | −4.07 |
| 69.70 | 7.86 | 12.19 | −4.33 | −4.37 |
| Temp. range 30–40°, mid. temp., °A. = 308.1 | | | | |
| 74.87 | 8.41 | 13.34 | −4.93 | −3.97 |
| 70.70 | 8.22 | 13.34 | −5.12 | −4.27 |
| 66.40 | 8.73 | 13.34 | −4.61 | −4.58 |

## Summary

The rate of reaction between iodide and persulfate ions was studied at 20, 30 and 40° in isodielectric and isocomposition ethyl alcohol–water media.

Measurements were made at various concentrations of potassium nitrate in ethyl alcohol–water media at a constant dielectric constant of 69.00 and for a fixed concentration of reactants. The salt effect measured in this solvent did not vary markedly from the predictions of the Debye–Hückel limiting law even for values of $\sqrt{\mu}$ = 0.212 and greater.

The energies of activation in the presence of the neutral salt increased with increasing temperature and decreased with increasing ionic strength. A similar trend was observed in the case of the frequency factor $B$.

An equation was derived for calculating the difference between critical increments measured in isocomposition media of a given dielectric constant and those measured in isodielectric media of any specified dielectric constant. Calculations of our data by this equation show that for the reaction between iodide and persulfate ions in ethyl alcohol–water solvent, the electrostatic influences

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(16) Laidler and Eyring, *Ann. N. Y. Acad. Science*, **39**, 303 (1940).

predominate. The difference between the frequency factors $B$ measured in isocomposition media and those in isodielectric media was calculated by the equation of Amis and Cook.[2]

The $r$ values used in the calculations of the difference between the critical increments and the difference between the frequency factors in the two kinds of media were identical. The $r$ value obtained from the slope of the line log $k_{\kappa=0}$ *versus* $1/D$ was almost twice that used in the above calculations.

University, Louisiana Received July 11, 1941

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[Contribution from the Chemistry Department of the University of California at Los Angeles and the Institute of Physical Chemistry at Charles University, Prague, Czechoslovakia]

# The Polarographic Reduction of Osmium Tetroxide

By W. R. Crowell, J. Heyrovsky[1] and D. W. Engelkemeir

The high valence state of osmium in osmium tetroxide and therefore the possibility of obtaining a comparatively large number of forms in its reduction renders a study of its polarographic reduction of particular interest. The purpose of the present paper was to conduct a study of the reduction of osmium tetroxide by use of the dropping mercury electrode with a view to determining how many steps are possible in this reduction, the identification of these steps, the conditions under which the compounds formed may be prepared, the approximate reduction potentials of the osmium couples involved and the analytical possibilities of such a process. The identification of the valence states of the various steps was accomplished by comparing the polarogram made with osmium tetroxide with that made with potassium osmate.

Preliminary experiments showed that it was not possible to conduct a polarographic reduction of osmium tetroxide or of quadrivalent osmium compounds in an acid solution because of the reduction of these compounds by mercury. Polarograms obtained in solutions of sodium, potassium, lithium and tetramethylammonium hydroxides did not show consistent and well-defined waves.[2] The best results were obtained with solutions of barium and calcium hydroxides. The curves shown in Figs. 2 and 3 were made by using saturated solutions of calcium hydroxide.

## Experimental

**Reagents.**—A potassium hydroxide solution of osmium tetroxide and crystals of potassium osmate, $K_2OsO_4 \cdot 2H_2O$, were prepared according to the methods recently described by one of the authors.[3] The calcium hydroxide solution of osmium tetroxide was prepared by acidifying the potassium hydroxide solution of the tetroxide with sulfuric acid and distilling the tetroxide into a saturated solution of lime water. The osmate solution consisted of potassium osmate dissolved in saturated lime water in an amount not sufficient to cause appreciable precipitation of calcium osmate. The solutions were filtered through a sintered glass filter to free them from calcium carbonate and were stored in glass stoppered bottles. The nitrogen used in freeing the solutions from air was first passed through a hydrochloric acid solution of chromous chloride. The mercury was purified by passing through a nitric acid washing tower, drying and distilling *in vacuo*. All chemicals were of reagent grade.

**Procedure.**—The apparatus in the early stages of the work consisted of a standard model of the Heyrovsky polarograph, while that used in the last stages was essentially of the same type with some modification in its mechanical details. With the latter apparatus was used a standard Leeds and Northrop galvanometer with a figure of merit of $4.9 \times 10^{-9}$ amp./mm./meter. The mercury capillary tube had a drop time of approximately three seconds. Nitrogen was bubbled through all solutions for thirty minutes before each run. Since it was found that even in the alkali solutions there was a small tendency for the mercury to react with the tetroxide, an apparatus of the type shown in Fig. 1 was used in which the anode and cathode compartments were separated by a short arm having a heavy 2-mm.-bore stopcock. The dropping mercury in the cathode compartment fell into a capillary tube, and was withdrawn from time to time in order to prevent overflowing from the capillary into the main body of the solutions. The stopcock between the two compartments was kept closed except during a run. The tetroxide solution previously freed from dissolved air was added to a saturated lime water solution by means of a Heyrovsky buret. The osmate solution, because of its instability, had to be prepared fresh for each run and was used in undiluted form. The anode consisted of mercury covered with a thin layer of mercuric oxide in contact with lime water saturated both with calcium hydroxide and mercuric oxide. The potential of this half cell at 25° has been shown by Samuelson and

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(1) War conditions within recent months have rendered communications with Dr. Heyrovsky impracticable, and therefore it has been necessary to carry out the final stages of this work and to write this article without the benefit of his collaboration.

(2) A portion of this part of the work was conducted by Mr. Frank J. Dolezal, a research student in chemistry at the University of California at Los Angeles.

(3) Wm. R. Crowell, Don M. Yost and John D. Roberts, This Journal, **62**, 2176 (1940).