

The Isothermal Salt Effect in the Iodine Clock Reaction¹

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In studies on the iodine clock or Landolt reaction Skrabal (1) observed that the addition of sodium sulfate to the mixture caused a negative temperature coefficient in the time of reaction, T . Other workers (2, 3, 4) found that T was also affected at constant temperature by the presence of added halides and reducing agents, entities entering the actual chemical reactions involved. Only one instance of the isothermal effect of a presumably chemically inert salt, potassium nitrate, on T has been found in the literature (4). For this case T was found, in general, to increase (at a decreasing rate) with increasing molarity of the mixture in added salt. However, in one short series of experiments (apparently overlooked by the authors) a definite maximum occurred in the data for T as a function of the molarity of added salt. The present paper reports the extension of studies on the isothermal salt effect to usage of lithium, sodium, potassium and magnesium sulfates.

Experimental

The following standard aqueous solutions were prepared: 2.336×10^{-2} M c. p. potassium iodate, soluble starch (10 g. per liter), 5 N sulfuric acid and 3.1733×10^{-2} M c. p. anhydrous sodium sulfite (4.0000 g. per liter). The sulfite solution, made up fresh just before use, was never kept for more than three hours. The starch suspension was prepared at intervals as needed while the iodate solution, as well as the acid solution, was made in one large batch sufficient for use in all runs. Lithium, sodium, potassium, and magnesium sulfate stock solutions of desirable concentrations were prepared from weighed quantities of the appropriate c. p. or U. S. P. grade (latter grade used only for some of the magnesium sulfate solutions) compounds and the concentrations were checked by comparison of the observed densities with those reported previously (5).

A series of runs was made for each sulfate stock solution. For this series, a standard oxidant stock solution was prepared by mixing 100 ml. of acid, 250 ml. of the iodate, 150 ml. of the starch suspension and sufficient water and/or sulfate stock solution (measured volume) to give a total volume of one liter. Individual oxidant samples in the series were prepared in advance from 50 ml. of standard oxidant stock solution, x ml. (measured) of sulfate stock solution and $(150 - x)$ ml. of water and were kept in stoppered flasks. For a particular run, the oxidant sample was transferred to a one-liter beaker and its temperature was adjusted to $25 \pm 1^\circ$ C. A reductant sample was then prepared separately by mixing 25 ml. of the sulfite solution, y ml. (measured)

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of the same sulfate stock solution, (170 — y) ml. of water and (after adjustment of the temperature as before) 5 ml. of the acid. The reductant sample was stirred vigorously for two or three seconds and poured rapidly into the oxidant. The mixture was stirred for five to seven seconds and then allowed to stand until the dark blue color developed.

For T less than thirty seconds development of the color was visually instantaneous throughout the solution and reproducibility was ± 0.3 seconds. For T more than about thirty seconds, appearance of a thin overlying dark blue layer in the solution preceded the homogeneous color change by as much as several seconds and the main coloration proceeded at a visually perceptible rate. For these greater values of T reproducibility was ± 0.6 seconds. All solutions used appeared clear except for those containing the higher concentrations of magnesium sulfate. The temperature of the mixture (checked after coloration) was $25.0 \pm 0.2^\circ$ C. in every case. Duplicate runs were usually made.

Results and Discussion

Comparative data for the effects of the four metallic sulfates used (in concentrations up to .47 M) are given in Table I. Since the three alkali sulfates were equivalent in their effects (within experimental error), data for higher salt concentrations were secured only for sodium and magnesium sulfates. From complete data for these two salts (Fig. 1), one observes that at least up to concentrations of 0.8 M

TABLE I. Effect of Concentration of Solution in Added Sulfate on Time of Reaction, T

Ml. of 0.622 M Sulfate Used in Sample*	T (in seconds) for Use of			MgSO ₄
	Li ₂ SO ₄	Na ₂ SO ₄	K ₂ SO ₄	
0	14.8	15.0	15.2	15.2
50	26.2	25.8	25.2	23.6
150	42.8	43.4	41.8	34.6
200	48.8	49.2	47.2	38.4
300	55.8	57.0	56.4	42.2

*Total volume of sample, 400 ml.

the time of reaction, T, increases, but at a decreasing rate, with increasing concentration of added salt, or, that is, with increasing ionic strength, μ , of the solution. The magnesium ion, however, is less effective than two sodium ions in regard to lengthening T. This difference is not explainable simply in terms of ionic strength, for on this basis alone the magnesium ion should be the more effective. Since Eggert has found (2) that T varies inversely as the approximate square of the hydrion concentration, it is possible that the overall salt effects observed here are the results of two opposing factors, namely (a) the

ionic strength or primary salt effect tending to cause T to increase with increasing molarity in all cases and (b) hydrolysis of the salt (a secondary salt effect) causing an increase in the hydron concentration and tending to cause T to decrease with increasing molarity. Hydrolysis should be operative only in the case of the magnesium salt where it might be sufficiently extensive as to overcompensate for the anticipated larger (as compared to the effect of the sodium salt) primary salt effect.

As one can see in Figure 1 or even more strikingly in Figure 2, a definite maximum is present in the curve for magnesium sulfate. Unfortunately the lower molar solubility of sodium sulfate prevented

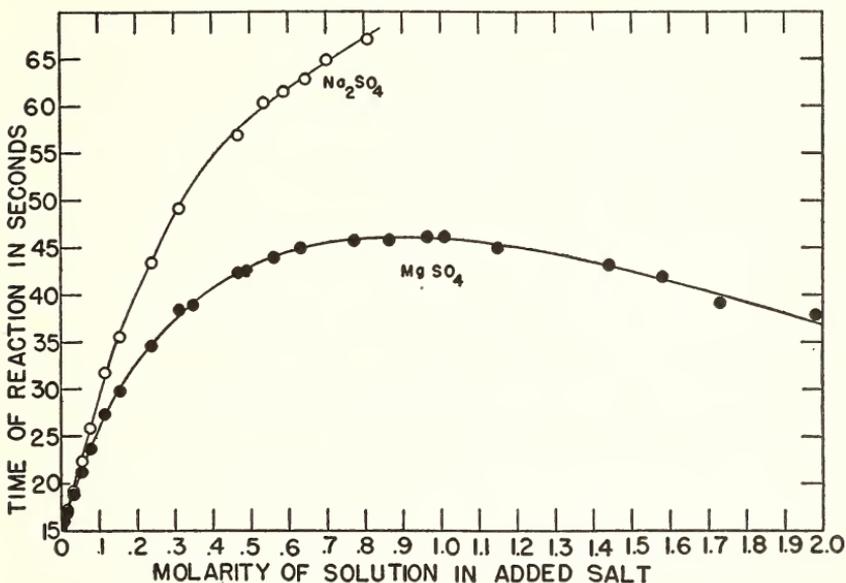
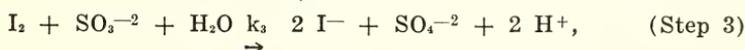
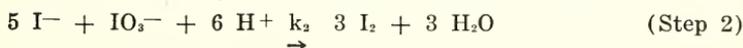
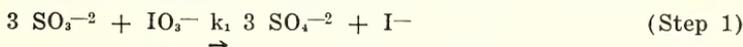


Fig. 1. Molarity of solution in added salt plotted against time.

further extension of data in order to search for such a maximum in the other curve. Information available for the salt potassium nitrate (4), indicates that this maximum is not a peculiarity associated with the magnesium ion, and, hence, may be a primary salt effect. This supposition gains plausibility when one examines the situation somewhat quantitatively.

As the result of some excellent experimental and theoretical endeavors by various people, Eggert (2, 3) proposed three major steps to the overall Landolt reaction. These are



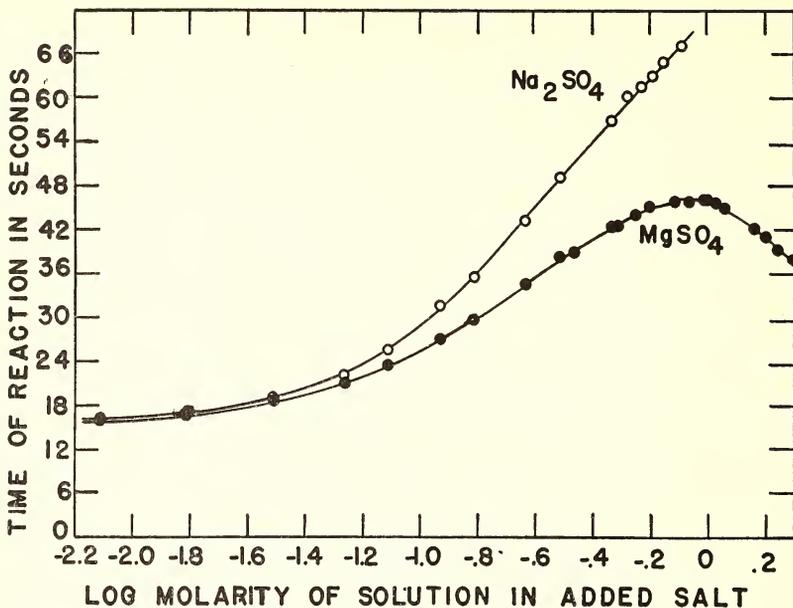


Fig. 2. Log molarity of solution in added salt plotted against time.

where the k 's are the specific rate constants for the respective steps and $k_3 > k_2$

$k_2 > k_1$. He found, moreover, that T was satisfactorily given by the semiempirical equation,

$$T = \frac{1}{k_2 - k_1} \ln \frac{k_2}{k_1} \quad (\text{Equation 1})$$

The effect on k of varying μ can be ascertained theoretically. Thus, for the reaction $A + B \rightleftharpoons X \rightarrow \text{Products}$, where A and B are the simplest entities involved in the rate-determining step of the reaction and X is the activated complex formed, k is given by the expression (6)

$$k = m \frac{f_A f_B}{f_X} \quad (\text{Equation 2})$$

where m is a positive constant and the f 's are the corresponding activity coefficients. Taking natural logarithms of both sides of equation 2 gives

$$\ln k = \ln m + \ln \frac{f_A f_B}{f_X} \quad (\text{Equation 3})$$

The last term of equation 3 can be evaluated from the expression for the complete Debye-Hückel theory (7)

$$\ln f = a \mu - \frac{bZ^2 \mu^{3/2}}{1 + c\mu^{1/2}} \quad (\text{Equation 4})$$

where a, b and c are positive constants and z is the electrical charge on the entity under consideration (A, B or X). Substituting $\mu^{1/2} = v$ in equation 4 and making use of the relationship $z_X = z_A + z_B$, one obtains

$$\ln \frac{f_{AB}}{f_X} = av^2 + \frac{2bz_Az_Bv}{1 + cv} \quad . \quad (\text{Equation 5})$$

Assuming that z_A and z_B are both negative for step 1 but opposite in sign for step 2, one finds (from equations 3 and 5)

$$\ln k_1 = \ln m_1 + av^2 + \frac{b_1v}{1 + cv} \quad (\text{Equation 6})$$

$$\ln k_2 = \ln m_2 + av^2 - \frac{b_2v}{1 + cv} \quad , \quad (\text{Equation 7})$$

where m_1 , b_1 , m_2 and b_2 are positive constants. Substituting for k_1 and k_2 from equations 6 and 7 in equation 1, one obtains

$$T = \frac{\ln \frac{m_2}{m_1} - \frac{(b_1 + b_2)v}{1 + cv}}{\quad} \quad . \quad (\text{Equation 8})$$

$$\exp av^2 \left[m_2 \exp \left(- \frac{b_2v}{1 + cv} \right) - m_1 \exp \left(\frac{b_1v}{1 + cv} \right) \right]$$

Evaluation of the limits for equation 8 shows that $\lim_{v \rightarrow 0} T = \lim_{\mu \rightarrow 0} T =$

a constant (as observed) and $\lim_{v \rightarrow \infty} T = \lim_{\mu \rightarrow \infty} T = 0$.

For small values of v (i. e. for dilute solution) equations 6 and 7 reduce to the simpler expressions

$$\ln k_1 = \ln m_1 + b_1v \quad \text{and} \quad \ln k_2 = \ln m_2 - b_2v$$

Hence, for this situation, k_1 increases with increasing μ while k_2 decreases simultaneously. These combined variations should cause T to increase with increasing μ (in dilute solution) since the increasing factor

$\left(\frac{1}{k_2 - k_1} \right)$ of equation 1 will overwhelm the influence of the

decreasing factor $\left(\ln \frac{k_2}{k_1} \right)$. This consideration, coupled with

those of the previously evaluated limits of T for infinitely dilute and infinitely concentrated solutions and the assumption that T is a continuous function of μ throughout this range, necessitates (in theory) the presence of at least one maximum in each curve for T versus concentration of added chemically inert salt.

Further experimentation is planned in an effort to elucidate this salt effect and to test the mechanistic details postulated here.

Summary

Lithium, sodium, potassium and magnesium sulfates have been found to increase the time of the iodine clock reaction at constant temperature when added in concentrations up to at least .47 M. Mole for mole the three alkali sulfates were equally effective. The curve of time versus concentration for the less effective magnesium sulfate showed a maximum. Interpretations of the results in terms of primary and secondary salt effects are presented.

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