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Kinetics Studies of the Reactions of $KMnO_4$ and of KIO_4 in Alkali Halide Disks

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The kinetics of the solid state reactions of $KMnO_4$ in alkali halide matrices and KIO_4 in alkali halide matrices were studied. All reactions were found to be first order with respect to the species being reduced. Rate constants were determined at 25, 50 and 100°C, and activation energies were determined for the reactions of $KMnO_4$ in KI and KIO_4 in KI. At 25°C, the rate constants for the reaction of $KMnO_4$ in KI and $KMnO_4$ in RbI were approximately the same. But the rate constant at 25°C for the reaction of KIO_4 with I^- was about 2½ times larger in a RbI disk than in a KI disk. Possible mechanisms for the solid state processes are suggested.

Introduction

Reports of kinetics studies in alkali halide matrices have been limited to thermal decompositions of organic compounds (*1–5*). Although reactions of sample with the alkali halide salt have been discussed (*5–11*), no studies of the kinetics of these reactions have been reported.

The reaction of $KMnO_4$ in alkali iodide disks was first noted by Manzelli and Taddei (*12*). Later, the nature of these reactions and the reactions of KIO_4 in alkali halide disks was studied (*7, 8*). This paper presents the results of kinetics studies of the reactions of $KMnO_4$ and of KIO_4 in some alkali halide disks.

The products of the reaction of $KMnO_4$ and KI are pH dependent in aqueous media. In basic solution, the products are IO_3^- (*13*) and either MnO_2 (*14*) or MnO_4^{-2} (*15*); while in acid solution, Mn(II) and I_2 (*14*) are produced and the kinetics have been studied (*16*). The kinetics of the reactions of $KMnO_4$ with KBr (*17*) and KCl (*18*) in aqueous solution have been reported also. There are no available studies of the kinetics of IO_4 with potassium halides in any reaction medium.

Experimental

Potassium bromide, spectrograde, was obtained from Matheson, Coleman and Bell. Rubidium iodide, ultrapure, was obtained from Alfa Inorganics. The other chemicals used in this study were obtained from Fisher Chemical Co. and were reagent grade. The alkali halide salts were heated at 110°C for at least one day before use in the preparation of the disks. Infrared spectra of the alkali halide salt after heating showed only a weak absorption due to the presence of water.

The grinding and mixing of all samples were carried out with a mortar and pestle for exactly 5 min. Pressed pellets from these samples were prepared using standard methods. All spectra were recorded from 4000–650 cm^{-1} on a Beckman IR-8 Infrared Spectrophotometer.

The base-line method was used to determine the initial and final percent transmittance of the peaks of interest and both were corrected for weight variations in the disk (*5*). Calibration curves of $KMnO_4$ in KI and KIO_4 in KI could not be obtained because immediate reactions occurred during the preparation of the disks (*7*). However, an extrapolation

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method has been developed which allows the estimation of calibration curves for these two systems (*19*).

Results and Discussion

The products of the reaction of $KMnO_4$ in a KI disk have been reported as KIO_4, which is then converted to KIO_3, and MnO_2 (*7*). The same products were observed with nujol mull as the reaction medium (*8*) and the reaction appears to be analogous to that occurring in a neutral aqueous medium (*15*). No reactions were observed in this study when $KMnO_4$ was dispersed in KBr and in KCl at room temperature. However, a reaction was attained when the disk containing $KMnO_4$ and KBr was heated at 100°C for 24 hr. The only observable product in the infrared spectrum was MnO_2. Since no oxides of bromine were detected, Br_2 is the other probable product. The reported products for the reaction of $KMnO_4$ with KBr in a strongly acid aqueous medium was Mn^{+2} and Br_2 (*17*).

The only observable product of the reaction of KIO_4 in KI is KIO_3, whereas for the reaction of KIO_4 in KBr, both KIO_3 and $KBrO_3$ are reported as products (*7*). The latter reaction in the disk occurs either by standing for several days at ambient temperatures or by heating the disks to 100°C for several hours (7).

Stoichiometry

The infrared spectra indicate that the permanganate ion is being reduced to MnO_2 while the iodide is being oxidized to periodate ion which is in turn converted to iodate ion. The reactions of KIO_4 in alkali halide disks were studied in order to elucidate the nature of the conversion of periodate ion to iodate ion. Potassium periodate might react in one of the following ways.

$$3IO_4^- + I^- \rightarrow 4IO_3^-, \qquad (1)$$

$$IO_4^- \rightarrow IO_3^- + \tfrac{1}{2}O_2, \qquad (2)$$

$$IO_4^- + 2I^- + H_2O \rightarrow IO_3^- + I_2 + 2(OH)^-. \qquad (3)$$

The concentrations of KIO_4 and KIO_3 were determined as a function of time for the reaction of KIO_4 in KI. The results show that the ratio of KIO_4 reacted to KIO_3 produced is 1.06. Furthermore, the KI disk containing KIO_4 shows a distinct coloration which becomes darker with time, indicating the presence of I_2 in the disk. Thus, the evidence suggests that the reaction in Eq. (3) is occurring when KIO_4 is dispersed in a KI matrix.

However, Eq. (3) may not represent the conversion of KIO_4 to KIO_3 in the KI disk containing $KMnO_4$. The infrared spectra show that in the initial stages of the reaction of $KMnO_4$ and KI, there is a definite time lag before MnO_2 begins to form. Furthermore, concentration–time data indicate that, for a given period of time, 10_3^- is forming at a faster rate in the reaction between $KMnO_4$ and KI than in the reaction between KIO_4 and KI. These results suggest that $KMnO_4$ is converted to MnO_2 through some intermediate state and this intermediate state may be participating in the conversion of KIO_4 to KIO_3. Such an intermediate could be Mn^{2+} which is known to act as a catalyst in reaction sequences where it is produced during the initial reactions (*20*). Thus, the reactions occurring in the KI disk containing $KMnO_4$ may be written as

$$8MnO_4^- + 5I^- + 12H_2O \rightarrow 8Mn^{2+} + 5IO_4^- + 24(OH^-), \qquad (4)$$

$$Mn^{2+} + IO_4^- + 2(OH^-) \rightarrow MnO_2 + IO_3^- + H_2O. \qquad (5)$$

The reactions of $KMnO_4$ and of KIO_4 with iodide ion were also carried out in RbI matrices. The spectra indicated that there were no essential qualitative differences between the reactions occurring in RbI. The stoichiometries appear to be independent of the nature of the cation in the alkali iodide disk.

Kinetics

Examination of all the kinetics data obtained in this study indicated that none of the reactions studied approached completion at infinite time. But the reactions did approach a steady state after a finite period of time. The equation for a first-order reaction that does not go to completion at infinite time can be written as

$$\ln[(A_0 - A_\infty)/(A - A_\infty)] = kt.$$

All the reactions were found to obey this first-order rate equation. This is shown in Figs. 1 and 2 for the $KMnO_4$–KI and KIO_4–KI systems, respectively. The systems studied and their corresponding rate constants are shown in Table I.

The energy of activation was determined for the $KMnO_4$–KI and KIO_4–KI systems. The values obtained for the systems were 3.97 kcal/mole for the reaction of $KMnO_4$ with KI and 5.93 kcal/mole for the reaction of KIO_4 with KI. The activation energy plots are shown in Fig. 3.

The uncertainties in the rate constants are probably in the range of 5–10%. In the following discussion, a maximum error of 10% in the values of the rate constants and the activation energies is assumed.

The results of this study indicate that the reactions of $KMnO_4$ with KI and KIO_4 with KI at 25°C have approximately the same rate constant. But the energy of activation for the KIO_4–KI system is higher than that for the $KMnO_4$–KI system. Also, the rate of the reaction between $KMnO_4$ and I^- appears to be only slightly dependent on the nature of the cation in the alkali iodide medium. But the reaction of KIO_4 with I^- is about $2\frac{1}{2}$ times faster in a RbI matrix than in a KI matrix.

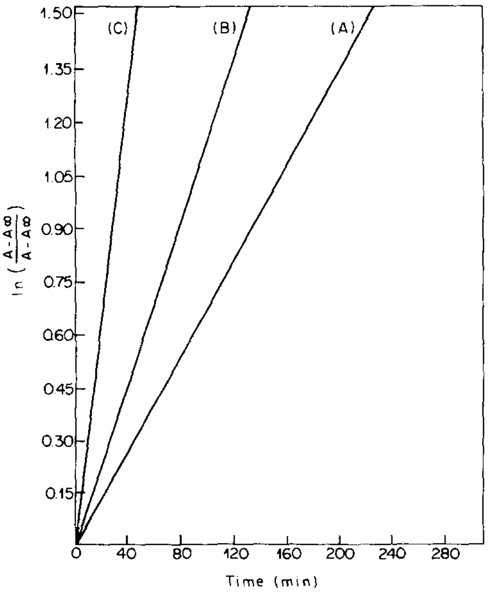

FIG. 1. First-order reaction plot for $KMnO_4$ in KI disk at (A) 25°C; (B) 50°C; (C) 100°C.

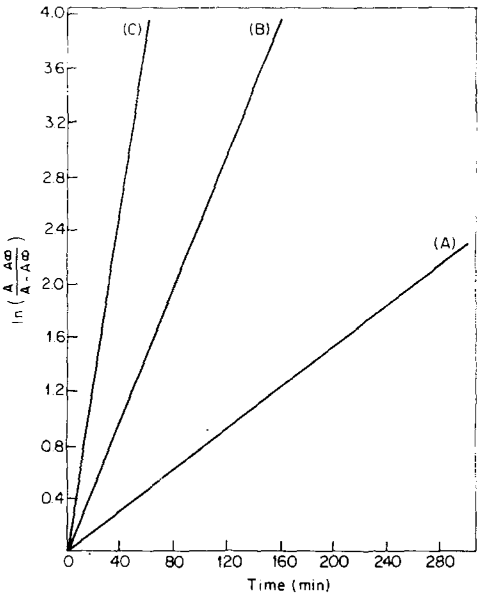

FIG. 2. First-order reaction plot for KIO_4 in KI disk at (A) 25°C; (B) 50°C; (C) 100°C.

Mechanism

The experimental evidence suggests that the mechanism for the solid state reaction of

TABLE I

REACTION RATE CONSTANTS FOR FIRST-ORDER REACTIONS OF $KMnO_4$ AND KIO_4 IN ALKALI HALIDE DISKS

System	Temp (°C)	$k \times 10^3$ (min^{-1})
$KMnO_4$ in KI	25	9.11
	50	15.6
	100	43.7
KIO_4 in KI	25	7.64
	50	24.8
	100	63.1
$KMnO_4$ in KBr	100	38.1
KIO_4 in KBr	100	17.9
$KMnO_4$ in RbI	25	6.82
KIO_4 in RbI	25	18.2

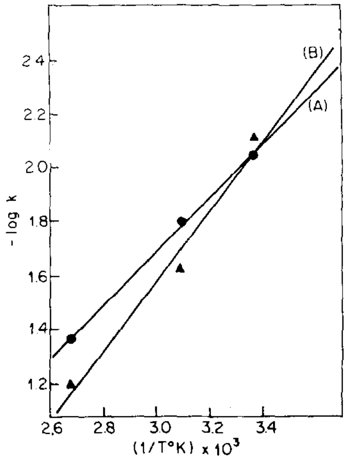

FIG. 3. Activation energy plots for the (A) $KMnO_4$/KI system; (B) KIO_4/KI system.

$KMnO_4$ in a KI disk differs from that for the reaction of KIO_4 in a KI disk. The results in Table I show that the rate of the permanganate ion–iodide ion reaction is only slightly dependent on the nature of the cation in the alkali iodide matrix. But the reaction of KIO_4 in a RbI disk is about 2½ times faster than the reaction in a KI disk. Furthermore, $KMnO_4$ does not react with KI (not dried in an oven) in a nujol mull unless 1–2 drops of water are added to the mull suspension (*8*). However, KIO_4 reacts with KI (not dried in an oven) in a mull without any external addition of water. As in the reactions of $KMnO_4$ with KI (*8*), KIO_4 appears to react in the same way with KI both in the disk and in the nujol mull.

Three possible mechanisms can be postulated for these reactions.

1. The stresses introduced in the pressing of the disk can cause rupturing of the crystal lattice followed by diffusion through the disk (*21*). The ease and extent of lattice rupture will be a function of the crystal lattice energies (*11*, *22*). The lattice energies decrease with increasing ionic radii (*22*), thus increasing the extent of lattice rupture and the rate of the solid state reaction occurring in the disk.

2. The alkali metal ion can be catalyzing the reaction by facilitating the formation of a transient–intermediate complex between the reductant and the oxidant that makes the electron transfer process occur faster. The order of the cationic catalytic ability would be expected to increase with an increase in ionic sizes, since the increasing polarizability of the ion would increase the ability of the ion to enhance the rate of electron transfer. Such behavior has been reported in the reactions of Ce(IV) with Sm(II) (*23*) and with Sb(III) (*24*) catalyzed by halide ion in aqueous media, where the catalytic ability of the halide ion increases from chloride ion to bromide ion.

3. The residual water in the disk could act as the reaction medium. Thus, ions in the crystal lattice would go into solution and react. There would be some ionic effects on the reaction rate, but these would be concentration effects. The nature of the spectator ions would have minimal effect on the rate of the reaction.

Since the rate of the reaction between IO_4^- and I^- depends on the nature of the cation in the matrix, the reaction path could involve mechanism 1 and/or mechanism 2. On the other hand, the experimental data suggest that the reaction between MnO_4^- and I^- could be proceeding by a path postulated in mechanism 3. The slight dependence of the rate on the nature of the cation in the alkali halide matrix could be a result of the salt effect in the solution.

More experimental work is necessary on on other reaction systems in alkali halide disks to fully evaluate the mechanism by which these solid state reactions occur. Work is now proceeding in this laboratory on the reactions of $K_2S_2O_8$ in alkali halide matrices.

It would also be desirable to learn why the nature of the reaction in the alkali halide matrix differs with different halide ions. For example, in aqueous acid solutions the reaction of $KMnO_4$ with halide ions produces the halogen molecule in all cases studied (*16–18*). However, in the disk, the reaction of $KMnO_4$ with KI produces KIO_4 and KIO_3, whereas the reaction of $KMnO_4$ with KBr produces Br_2. The reaction of KIO_4 in KBr yields KIO_3 and $KBrO_3$ (*7*) but the reaction of KIO_4 in KI yields KIO_3 and I_2. Furthermore, the reaction of $KClO_4$ in KBr yielded only $KClO_3$ (*6*) but the reaction of $KClO_4$ in KI produced $KClO_3$ and KIO_3 (*6*).

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