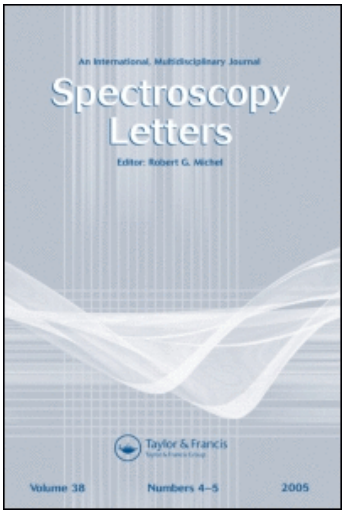

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Quantitative Determination of Reactive Species in Alkali Halide Disks

Don G. Lambert[a]; Howard S. Kimmel[a]
[a] Department of Chemical Engineering and Chemistry, Newark College of Engineering, Newark, New Jersey

To cite this Article Lambert, Don G. and Kimmel, Howard S.(1972) 'Quantitative Determination of Reactive Species in Alkali Halide Disks', Spectroscopy Letters, 5: 11, 415 — 419
To link to this Article: DOI: 10.1080/00387017208065410
URL: http://dx.doi.org/10.1080/00387017208065410

SPECTROSCOPY LETTERS, 5(11), 415-419 (1972)

QUANTITATIVE DETERMINATION OF REACTIVE SPECIES IN ALKALI HALIDE DISKS

KEY WORDS: Infrared spectroscopy, alkali halide disks, quantitative analysis

Don G. Lambert and Howard S. Kimmel
Department of Chemical Engineering and Chemistry
Newark College of Engineering
Newark, New Jersey 07102

As part of an infrared investigation of the kinetics of the reactions of $KMnO_4$ in a KI disk and of KIO_4 in a KI disk, the stoichiometry of the two reactions was needed. A previous study[1] has shown that MnO_4^- reacts in a KI matrix to produce IO_4^- (which then reacts further to form IO_3^-) and MnO_2. Iodate ion is the only observable product in the reaction of IO_4^- in a KI matrix[1]. The infrared absorption at $740cm^{-1}$, which is due to the presence of IO_3^-, was found to obey the Beer-Lambert Law. However, calibration curves for $KMnO_4$ in KI and for KIO_4 in KI could not be obtained because both species reacted with the dispersing medium during the preparation of the disk[1]. It was also observed that no immediate reaction occurred when KBr or KCl disks containing $KMnO_4$, or KIO_4 were prepared. Thus, an extrapolation method was sought which would permit the estimation of calibration curves for the reactive species.

EXPERIMENTAL

All the chemicals used in this study except KBr were obtained from Fisher Chemical Co. and were reagent grade. Potassium bromide, spectrograde, was obtained from Matheson, Coleman and Bell. The grinding and mixing of all samples were done with mortar and pestle. Pressed pellets from these samples were prepared using standard methods.

All spectra were recorded on a Perkin-Elmer 457 Infrared Spectrophotometer. The base-lime 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[2].

RESULTS

Calibration curves for KIO_3 in KCl, KBr, and KI are shown in Figure 1. Since these plots obey the Beer-Lambert Law, the slopes of the lines yield the extinction coefficients. It is seen that the extinction coefficients decrease going from the KI matrix to the KCl matrix. Calibration curves for $KMnO_4$ in KCl and KBr (Absorption band at $900cm^{-1}$ was used.) and for KIO_4 in KCl and KBr (Absorption band at $847cm^{-1}$ was used.) also obeyed the Beer-Lambert Law. The extinction coefficients obtained from calibration curves thus far discussed are shown in Table 1.

Hester and Krishnan[3] have reported that the vibrational frequencies for metal nitrates are linearly related to the ionic potential (z/r) of the metal ion. The linear relationship between the integrated absorption coefficient and the vibrational frequency[4] suggests that a similar relation may exist between the extinction coefficient of an infrared band and the

TABLE 1

Extinction Coefficient (cm^{-1}) of $KMnO_4$, KIO_4, and KIO_3 in Alkali Halide Disks

Alkali Halide substance	KI	KBr	KCl
KIO_3	7.34	5.25	2.92
KIO_4	7.95*	5.25	3.13
$KMnO_4$	1.24*	3.41	9.40

*Extrapolated value.

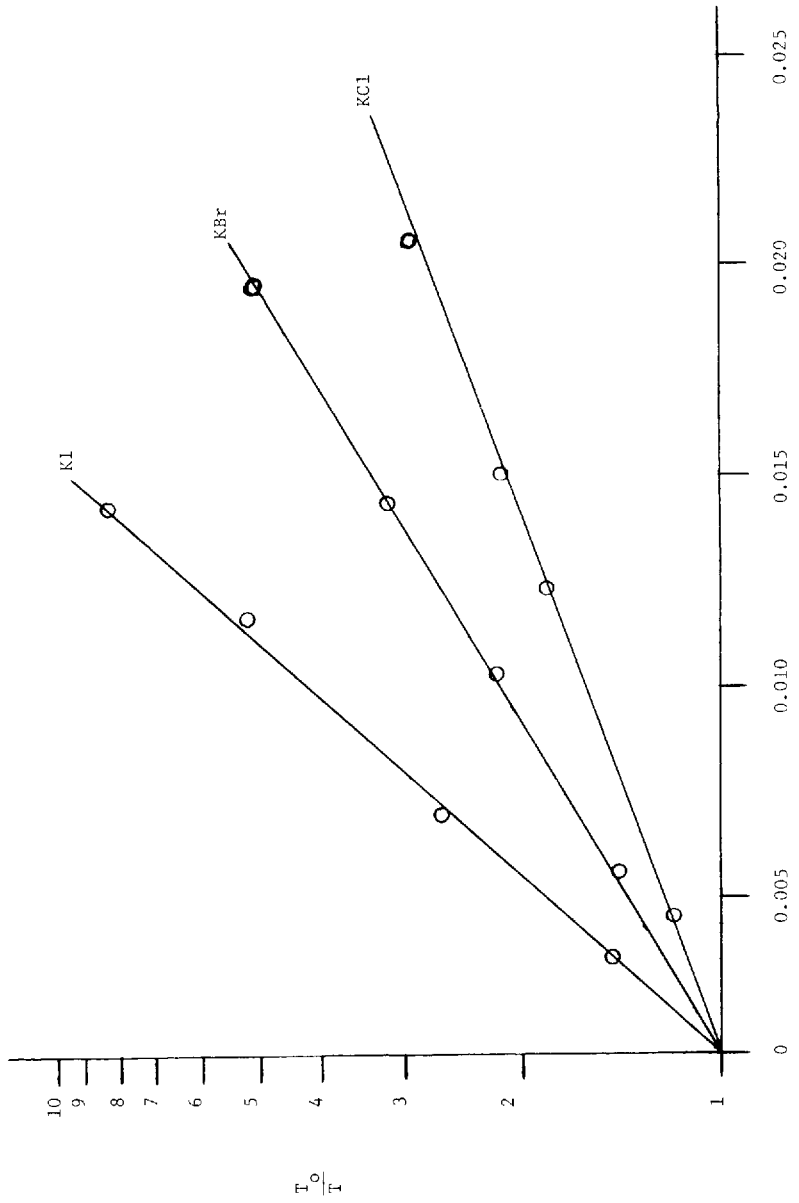

FIG. 1

Calibration Curves of KIO_3 in KCl, KBr, and KI.

reciprocal of the ionic radius; i.e., 1/r, of the negative ion making up the matrix, e.g., Cl^-, Br^-, and I^-.

A plot of the extinction coefficients of KIO_3 in KCl, KBr, and KI versus the reciprocals of the ionic radii of the respective negative ions was linear, as shown in Figure 2. If it is assumed that such plots for $KMnO_4$ in KCl and KBr and for KIO_4 in KCl and KBr are linear, then the extinction coefficients for $KMnO_4$ in KI and KIO_4 in KI can be estimated and calibration curves for these systems can be constructed. These estimated extinction coefficients are shown in Table 1.

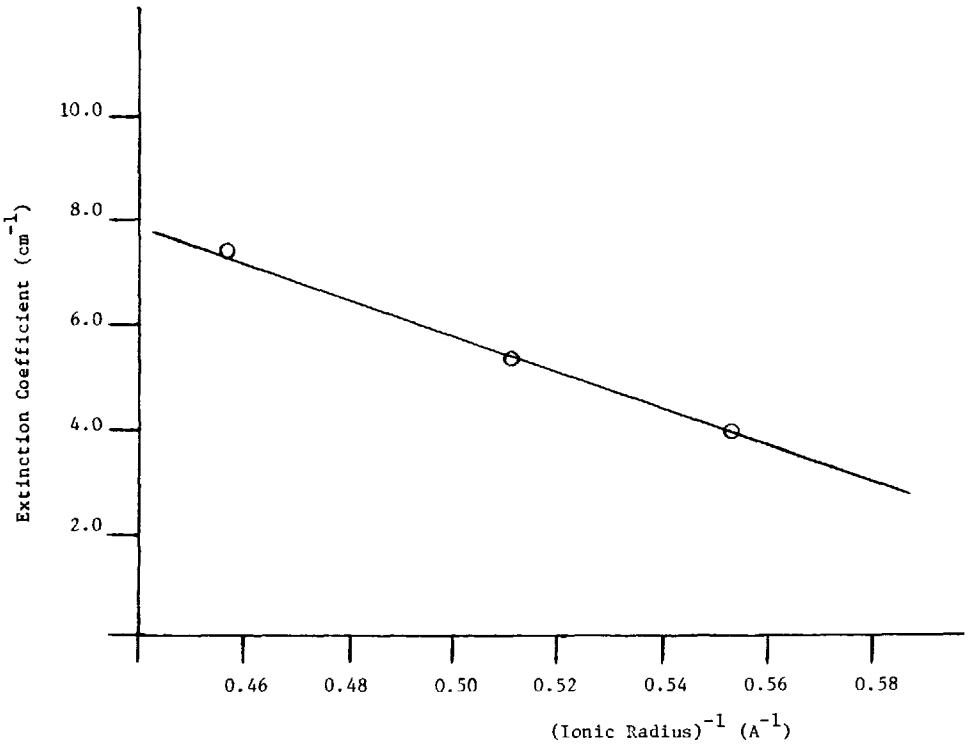

FIG. 2

Extinction Coefficients Vs. (Atomic Radius)$^{-1}$ of Negative Ion For KIO_3 in KCl, KBr, and KI.

The calibration curves obtained in this study for $KMnO_4$ in KI, KIO_4 in KI, and KIO_3 in KI were used to determine the concentrations of these species at various times during the course of the reaction. The consistency of the results obtained in the study of the stoichiometry of the reactions of interest and the work of Hester and Krishnan[2] suggests that the extrapolation method discussed in this communication should yield reliable extinction coefficients when the substance to be studied is not stable in an alkali halide matrix and calibration curves can not be obtained in the conventional manner.

REFERENCES

1. T. Gymkowski, D. G. Lambert and H. S. Kimmel, J. Inorg. Nucl. Chem., 34, 1841 (1972).

2. L. A. Cosby, "Vibrational Assignments for Solid Malonic Acid", Ph.D. Dissertation, West Virginia University, Morgantown, W. Va., 1970.

3. R. E. Hester and K. Krishnan, J. Chem. Phys., 47, 1747 (1967).

4. G. M. Barrow, "Introduction to Molecular Spectroscopy", McGraw-Hill Book Company, Inc., New York, 1962, p. 77.

Received September 28, 1972

Accepted October 16, 1972