TABLE III

THE RATE CONSTANT k' FOR THE OXIDATION OF SULFONES AT 80°

Original substrate	Concn., M	k', hr.$^{-1}$	k_0', hr.$^{-1}$
Diethyl sulfide	0.02	0.69	0.42
	.02	.67	.40
Diethyl sulfoxide	.02	.61	.34
	.01	.63	.36
Thiodiglycol sulfoxide	.01	.56	.29

reactions studied in this investigation. The results are presented in Table IV.

TABLE IV

ACTIVATION ENERGIES

Substrate	Concn., M	k_0, hr.$^{-1}$ 30°	80°	Act. en., kcal./mole
Water	55.5	0.0176	0.274	32.1
Diethyl sulfoxide	0.02	.090	.81	25.6
Thiodiglycol sulfoxide	.01	.090	.72	24.2
Diphenyl sulfoxide	.0075	.0076	.063	24.7

It is seen that the activation energy for the oxidation of the sulfoxides is nearly the same for the three compounds studied, and they are considerably less than the value for the oxidation of water. The average value of 24.8 kcal. for the three sulfoxides may be compared with the 26 kcal. observed in the persulfate oxidation of mercaptans.[3] The value for the water reaction is quite close to the average value of 34 kcal., which may be estimated from the data obtained by previous investigators under similar conditions.[6,8,9]

Effect of Oxygen on the Rate.—Two kinetic runs were made in which the reaction mixture was saturated with pure nitrogen and kept under an atmosphere of the gas throughout the experiment (Table II). The fact that the rate under these conditions is identical with those obtained in the presence of atmospheric oxygen indicates that the reaction is neither inhibited, retarded nor accelerated by oxygen. This affords evidence, though not of a conclusive nature, against a radical chain-type mechanism for the reactions studied.

Effect of Structure of the Compound Oxidized.—It is apparent from Fig. 2 and Table II that at 80° the oxidation of diethyl sulfoxide proceeds at a slightly faster rate than that of thiodiglycol sulfoxide, and that both of these compounds are oxidized much more rapidly than is diphenyl sulfoxide. These results are similar to those observed in the oxidation of sulfides by potassium persulfate[4] and by hydrogen peroxide.[15]

It would appear that an inductive effect is operative when a hydroxy, phenyl or chloro[15] group is present in the molecule close to the sulfur atom. By attracting electrons, negative groups such as these can effectively decrease the electron density at the sulfur atom, thus rendering the electrons less available for formation of a coördinate bond with an oxygen atom or for extraction by an oxidizing agent.

Effect of Sulfoxide Concentration.—Over the range of concentration studied in the above experiments, the rate of disappearance of persulfate is apparently independent of the concentration of the sulfur compound oxidized. The effect of much lower concentrations of sulfoxide on the rate will be presented in a future paper.

[15] K. Ishida, *J. Chem. Soc. Japan*, **64**, 242 (1943).

PHILADELPHIA, PENNA.

[CONTRIBUTION NO. 270 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE[1]]

Metal–Water Reactions. II. Kinetics of the Reaction between Lithium and Water Vapor

BY BRUCE E. DEAL AND HARRY J. SVEC

RECEIVED AUGUST 21, 1953

The rate of the reaction between lithium metal and water vapor has been studied from 45.0 to 75.0°. The reaction was found to proceed according to a logarithmic rate law. The rate constant was independent of water vapor pressure over a range of 22 to 55 mm. The energy of activation for the reaction was found to be 6.2 to 5.5 kcal./mole, depending on the water vapor pressure.

Introduction

The kinetics of metal–gas reactions involving O_2, N_2 and H_2 have been widely studied and numerous references are available.[2] However, few studies have been reported on water vapor–metal reactions and none using the more active metals.

A study of the rate at which reaction takes place between lithium and water vapor was undertaken as the second in a series which compares water vapor–metal reactions with other gas–metal reactions. Since the lithium reaction takes place according to the equation

$$2Li + 2HOH = 2LiOH + H_2$$

the rate of reaction was followed by observing the evolution of H_2 as a function of time under several water vapor concentrations.

It has been observed that the reaction of a gas with a metal may proceed according to one of several laws[3]

(I) the linear law $w = kt$

(II) the parabolic law $w^2 = kt$

(III) the logarithmic law $w = k \log (1 + at)$

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

[2] O. Kubaschewski and B. E. Hopkins, "Oxidation of Metals and Alloys," Academic Press, Inc., New York, N. Y., 1953.

[3] E. A. Gulbransen, *Trans. Electrochem. Soc.*, **91**, 573 (1947).

where w is the extent of reaction in time t, and k and a are constants. The latter two laws have been derived on the assumption that diffusion through the growing coat on the metal surface is the rate determining step of the reaction.[4,5] The diffusing species may be the positive or negative ions or even electrons.

Experimental

Rods of lithium metal were obtained from the Metalloy Corporation of Minneapolis, Minn. Spectrographic analysis indicated that the total impurities were less than 0.1% occurring as a mixture of Al, Ba, Ca, Mg, Mn and Si. Cylinders approximately 2 inches in length and slightly less than one-half inch in diameter were prepared by machining under sodium-dried turbine oil. Machining conditions were carefully controlled and repeated for each cylinder to ensure a uniform metal surface for the entire group of samples used in this study. As a result of these precautions, a smooth-appearing, shiny surface was obtained on the cylinders with no apparent tarnishing. The freshly machined cylinders were stored under sodium-dried turbine oil until introduced into the reaction apparatus.

Immediately preceding use, the dimensions of each cylinder were measured with machinists' calipers. The oil in which the lithium had been stored was removed by a rinse of sodium-dried petroleum ether followed by one of sodium-dried diethyl ether. During this latter rinse, a stainless steel hook was fastened to the top of the cylinder, by means of which the cylinder could be hung in the reaction vessel. The vessel was flushed with argon gas, the lithium cylinder placed in position in the vessel, and the system sealed with Apiezon W wax and immediately evacuated. Evacuation was continued for 30 minutes during which time the apparatus was partially immersed in a constant temperature bath. A series of experiments showed that in this time thermal equilibrium of the lithium with the bath was nearly attained. The apparatus was then closed to the vacuum source and completely lowered into the bath. When water vapor was introduced into the reaction vessel thermal equilibration was completed before the first pressure observation was made.

Lithium chloride solutions of several different concentrations were prepared for the purpose of varying concentration of the water vapor in contact with the lithium metal. The vapor pressure of each solution was determined at the experimental temperatures in the reaction vessel by means of a recording mercurial manometer.[6] Two ml. of lithium chloride solution was added through a mercury-covered serum-bottle rubber stopper by means of a hypodermic syringe. As the reaction between water vapor and lithium proceeded, the pressure of the hydrogen evolved was continually followed on the recording manometer. Observations were made at ten degree intervals from 45.0 to 75.0°.

Values for the weight per unit area of water vapor undergoing reaction were obtained from hydrogen pressures by determining the total volume of the reaction apparatus and the volume and surface area of the lithium cylinders. The hydrogen pressures were obtained by subtracting from the total pressure the vapor pressures of the LiCl solutions at the temperature being studied. It was assumed that the lithium surface areas obtained from the cylinder dimensions and used in these calculations were only minimum areas, but that they were proportional to the true areas by a constant factor. The reproducibility of the experimental results supported this assumption.

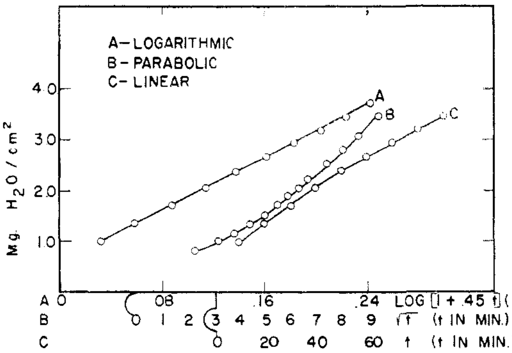

Fig. 1.—Comparison of three reaction rate laws for gas-metal reactions using water vapor–lithium data.

Results

Since the reaction of lithium with water vapor proceeds with the formation of a surface film, the reaction rate data are expected to fit one of the three gas–solid reaction rate laws, I, II or III. A comparison of these three laws is presented in Fig. 1 from which one may obtain the law which best describes the data for a typical reaction. The weight of water consumed (in mg. per cm.^{2} of lithium surface) is plotted against the appropriate function of the time. It is evident that a straight line is formed for the logarithmic treatment of the data while both the parabolic and linear plots are curved. Similar plots of data from other reactions corroborate this conclusion.

The value of the constant a in the logarithmic equation III was set equal to 0.4 by Brodsky and Cubicciotti[7] in silicon–oxygen reaction rate studies, but its magnitude under the conditions of this research was empirically determined by finding that value which best fitted the experimental data. A value of 0.45 for the constant a fits these data best.

Graphs were prepared for each reaction with mg. H_2O per cm.^{2} plotted against log $(1 + 0.45t)$, where t is time in hours. Values of the logarithmic rate constants k were obtained from the slopes of the initial part of the curves. In order that the vapor pressure effect on the reaction rates might be determined, reactions were run at 45.0 and 55.0 under various water vapor pressures. Plots of the data obtained in these experiments indicated that there is a certain water vapor pressure, about 55 mm., below which no further decrease in rate of reaction is observed. This fact was further in evidence when plots were made of rate constants *versus* temperature. At those temperatures where the water vapor pressure began to exceed the limiting vapor pressure mentioned above, deviation from a smooth curve appeared. An extrapolation of ten degrees beyond the point of deviation was made in order to estimate what the rate constant would be if there were no pressure effect. That this extrapolation was justified is indicated in Fig. 3. It is very probable that there is a lower limit to the pressure-independent region similar to what has been observed several times in oxygen–metal studies.[3] In the lithium–water vapor studies made here this effect was not observed since the lowest vapor pressure employed was 22 mm.

Typical examples of the rate plots are shown in Fig. 2 for the reaction data obtained between the temperatures 45.0 to 75.0° for two pressure ranges, 50 and 100 mm. It should be noted that on extending the data in Fig. 2 over a longer time, definite changes or breaks were observed in the slopes of the curves, appearing at a time corresponding to a certain reaction product coat thickness. These sudden breaks were dependent on temperature and pressure, but the rate of reaction became completely unpredictable.

The activation energy for the lithium–water vapor reaction was determined by plotting log k against $1/T$ and determining the slope, where k is the rate constant and T the absolute temperature.[8] Figure 3 shows this plot taken from reaction data for two different water vapor pressure ranges. It is observed that two straight lines are formed, the slopes of which have similar values. From the figures, values for the activation energy of the reaction are estimated to be 6.2 and 5.5 kcal./mole when the water vapor pressures are 50 and 100 mm., respectively. Since the difference between these two values cannot be explained solely upon the basis of experimental error, it must be concluded that there is a pressure effect which influences the activation energy of this reaction.

Discussion

The logarithmic rate law has been associated with glassy-appearing surface coatings by Brodsky

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[4] (a) N. B. Pilling and R. E. Bedworth, *J. Inst. Metals*, **29**, 529 (1923); (b) C. Wagner and K. Grunewald, *Z. physik. Chem.*, **40B**, 455 (1938).

[5] N. F. Mott, *Trans. Faraday Soc.*, **36**, 472 (1940).

[6] H. Svec and D. Gibbs, *Rev. Sci. Instruments*, **24**, 202 (1953).

[7] M. B. Brodsky and D. Cubicciotti, THIS JOURNAL, **73**, 3497–3499 (1951).

[8] J. S. Dunn, *Proc. Roy. Soc.* (*London*), **111A**, 203 (1926).

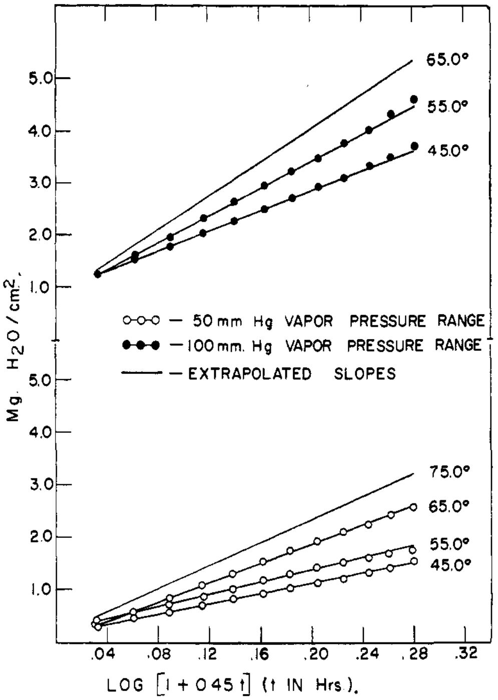

Fig. 2.—Logarithmic plot of water vapor data in two pressure ranges.

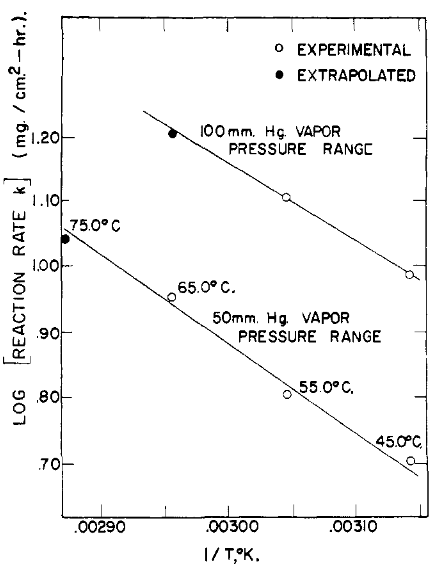

Fig. 3.—Log k vs. $1/T$ from water vapor–lithium data; each point represents the mean of several determinations.

and Cubicciotti.[7] These workers derived the equation from Fick's law following the method of Tammann and Koster,[9] assuming that the logarithmic oxidation was related to a vitreous oxide product. Therefore, it was interesting to note that in the reaction of lithium with water vapor, a glassy black coat always appeared on the metal surface at the beginning of the reactions. This black coat remained for a period of time depending on the temperature and water vapor pressure, and then slowly changed to a white material. Analysis of both the white and black material by means of an X-ray diffractometer indicated that the only compound present was LiOH. However, the glassy black coat was characterized in the X-ray patterns by broad peaks and absences of some reflections, indicating that a completely crystalline hydroxide was not formed during this stage of the reaction. Following the suggestion of Cubicciotti and Brodsky[7] this lack of crystallinity of the LiOH coat could be responsible for the logarithmic rate law observed for these data.

AMES, IOWA

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[9] G. Tammann and W. Koster, *Z. anorg. allgem. Chem.*, **123**, 196 (1922).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

Evidence for the Existence of an Ammine of Platinum(0)[1]

BY GEORGE W. WATT, M. T. WALLING, JR., AND PEGGY I. MAYFIELD

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The reduction of tetrammineplatinum(II) bromide with potassium in liquid ammonia at its boiling point is best interpreted as involving the addition of two electrons to the 4-coplanar tetrammineplatinum(II) ion to form a neutral tetrammine of platinum(0). Decomposition of this product yields only ammonia and platinum; the latter is an effective catalyst for the hydrogenation of olefins. The interaction of tetrammineplatinum(II) bromide and potassium amide in liquid ammonia yields platinum(II) amide 2-ammonate.

The reduction of salts of transitional metals by means of solutions of alkali metals in liquid ammonia typically results in *rapid* reduction to the elemental metals, in some cases accompanied by products of competing reactions, *e.g.*, amides, imides and/or nitrides.[2-5] The principal ammonia-insoluble product is usually a black finely divided solid that is pyrophoric and an excellent catalyst for the conversion of alkali metals to the corresponding amides and for the hydrogenation of olefins.[5]

The reduction of tetrammineplatinum(II) bromide, however, with potassium in liquid ammonia at −33.5° proceeds relatively slowly without evolution of water-insoluble gases and results in the precipitation of a yellowish-white voluminous solid that does not catalyze appreciably the formation of potassium amide. Although this primary reduction product ultimately decomposes to yield finely divided elemental platinum which is an excellent catalyst for alkali amide formation and for

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[1] This work was supported in part by the Office of Naval Research, Contract N6onr-26610.

[2] G. W. Watt, *Chem. Revs.*, **46**, 289 (1950).

[3] G. W. Watt and W. A. Jenkins, Jr., THIS JOURNAL, **73**, 3275 (1951).

[4] G. W. Watt and C. W. Keenan, *ibid.*, **74**, 2048 (1952).

[5] G. W. Watt, W. F. Roper and S. G. Parker, *ibid.*, **73**, 5791 (1951).