Another hypothesis that adequately describes the results is that of crack formation in the water polished surfaces by an activated process. When an interior crystal plane is converted into a surface plane by dissolution of the planes above it, a nonequilibrium system results. Because the equilibrium spacing is of the order of 6% smaller in the surface plane than in the interior,⁹ the surface so formed will be under tension. The tendency will thus be toward contraction and the dissipation of the strain energy by the formation of new surface in cracks. The possibility of crack formation of this type was first suggested by Lennard-Jones.⁹

(9) J. E. Lennard-Jones and B. M. Dent, Proc. Roy. Soc. (London), 121, 247 (1928).

The tendency for the linear defects to align themselves at preferred angles may be interpreted as due to the formation of cracks along planes of low free energy. An electron diffraction study of both heat treated and X-irradiated NaCl¹⁰ has also given evidence that these treatments result in crystallographic changes in the surface layers. Further work is needed to relate these observations to the results of this investigation.

Acknowledgments.—The authors would like to thank Dr. S. L. Simon for many helpful discussions during the course of this work and Dr. L. A. Girifalco for suggestions concerning the preparation of this paper.

(10) H. Leider, private communication.

HOMOGENEOUS CATALYTIC ACTIVATION OF MOLECULAR HYDROGEN IN AQUEOUS SOLUTION BY SILVER SALTS

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In aqueous solution, salts of silver were found to activate molecular hydrogen homogeneously as evidenced by their catalytic effect on the reduction of $Cr_2O_7^-$ and Ce^{+++} by H_2 . The kinetics are represented by: $-d[H_2]/dt = k[Ag^+]^2[H_2]$, where $k = 4.0 \times 10^9$ exp [-15,800/RT] liter² mole⁻² sec.⁻¹, in perchlorate solution. A mechanism is proposed involving a termolecular rate-determining step, in which an H_2 molecule reacts simultaneously with two Ag^+ ions thereby becoming activated. The results are compared with those obtained earlier for the activation of H_2 by Cu^{++} and Hg^{++} salts. It is concluded that the activation process may involve the simultaneous transfer of two electrons from the H_2 molecule to the catalyst.

Introduction

Recent work in this Laboratory has revealed a number of systems in which molecular hydrogen, in aqueous solution, is apparently activated homogeneously by interaction with a dissolved metal ion or metal-containing complex. In particular, such activity has been demonstrated for certain cupric¹ and mercuric² salts, as evidenced by the fact that these salts are reduced homogeneously by H_2 and, in some cases, can act as catalysts for the homogeneous hydrogenation of other dissolved compounds such as dichromate and ceric salts.

The present paper describes an extension of these studies to certain salts of the univalent metal ion, Ag^+ . Some indications that silver salts may activate hydrogen have been provided by earlier observations on the formation of metallic silver by hydrogen treatment of aqueous solutions of silver salts³ and on the absorption of hydrogen by silver permanganate solutions.⁴ However no detailed investigations of such systems appeared to have been made, particularly under conditions where complications arising from possible heterogeneous reactions were absent. Hence the essential nature of the homogeneous interaction between H₂ and

(1) (a) J. Halpern and R. G. Dakers, J. Chem. Phys., **22**, 1272 (1954); (b) R. G. Dakers and J. Halpern, Can. J. Chem., **32**, 969 (1954); (c) E. Peters and J. Halpern, *ibid.*, **33**, 356 (1955); (d) E. Peters and J. Halpern, THIS JOURNAL, **59**, 793 (1955).

(2) (a) J. Halvern, G. J. Korinek and E. Peters, *Research (London)*,
 7, S61 (1954); (b) G. J. Korinek and J. Halpern, THIS JOURNAL, 60, 285 (1956).

(3) M. N. Beketoff, Compt. rend., 48, 442 (1859).

(4) (a) F. Hein and W. Daniel, Z. anorg. Chem., 181, 78 (1929);
(b) F. Hein, W. Daniel and H. Schwedler, *ibid.*, 233, 161 (1937).

Ag⁺ remained to be elucidated. Recently the homogeneous activation of hydrogen in pyridine solution by silver acetate has been reported.⁶

In the present study, a procedure similar to that used earlier to study the activity of cupric salts,^{1d} was adopted, *i.e.*, the ability of Ag^+ to activate hydrogen homogeneously was determined by measuring its catalytic effect on the reaction between H₂ and $Cr_2O_7^-$ under conditions where no metallic silver was formed. Most of the measurements were made in perchlorate solution in which Ag^+ is believed to be essentially uncomplexed.

Experimental

C.r. grade chemicals were used throughout. $K_2Cr_2O_7$, NaOH, HClO₄, HNO₃ and AgNO₃ were obtained from Nichols Chemical Co. AgClO₄, NaClO₄ and Ce(ClO₄)₄ were G. F. Smith Co. products. H₂ and N₂ gases were supplied by Canadian Liquid Air Co.

The experimental solutions were prepared by mixing aliquots of standardized stock solutions of the various reagents in desired proportions and diluting with distilled water. Mixtures containing AgClO₄ were first boiled and filtered through sintered glass to remove any AgCl which might result from the presence of traces of chloride impurities in the perchlorate reagents.

Indicates in the perchlorate reagents. The final solutions were analyzed for $Cr_2O_7^-$ with a Beckman DU spectrophotometer using the 3500 Å, peak. Corrections were applied for the slight variation of optical density with acid concentration and for the small absorption of the reaction product, Cr^{+++} . The concentration of Ag⁺ was determined by titration with KCNS using a ferric indicator. Where Ce^{++++} was used (in place of $Cr_2O_7^-$) its concentration was measured volumetrically by adding an excess of standardized FeSO₄ solution and back-titrating with Ce(HSO₄)₄.

(5) L. Wright, S. Weller and G. A. Mills, THIS JOURNAL, **59**, 1060 (1955).

The glass reaction apparatus was completely immersed in a water-bath whose temperature was controlled to $\pm 0.03^{\circ}$. The H₂ gas was first passed through an aqueous NaNO₃ solution (of approximately the same ionic strength as the reacting solution) to saturate it with water vapor, and then dispersed, through a sintered glass plate, into a flask containing the reacting solution (250 ml.). To follow the reaction, samples of the solution were withdrawn periodically during the experiment, quenched by cooling in an ice-bath, and the concentration of unreacted $Cr_2O_7^-$ (or Ce^{++++}) determined as described earlier. Prior to introducing the H₂, the apparatus was placed in the water-bath and allowed to remain for about 30 minutes while attaining thermal equilibrium. The solution was sampled and analyzed during this period to ascertain that it was completely stable in the absence of hydrogen. Zero reaction time, recorded at the instant that the flow of H₂ was commenced, may be subject to an uncertainty of up to a few minutes because of the time required for the solutions to become saturated with H₂.

The atmospheric pressure was recorded during the experiment and the H₂ partial pressure was calculated by subtracting the solution vapor pressure (estimated from available data for comparable NaClO₂ solutions). Different H₂ partial pressures were achieved, in a series of experiments designed to determine the effect of this variation, by using H₂-N₂ gas mixtures of various proportions. These mixtures were analyzed for H₂ by combustion over CuO.

Results

In the presence of AgClO₄, $Cr_2O_7^{-6}$ was found to react with H₂, over a wide range of conditions, according to the following stoichiometric relation

$$Cr_2O_7^- + 3H_2 + 8H^+ \longrightarrow 2Cr^{+++} + 7H_2O \quad (1)$$

In no case could any change in the Ag⁺ concentration be detected, nor was there any indication of formation of metallic silver, until after the reduction of $Cr_2O_7^-$ had gone to completion.

A series of typical rate plots, representing the disappearance of Cr₂O₇⁻ according to the above reaction, are shown in Fig. 1. The rate is seen to be essentially of zero order with respect to the changing concentration of Cr_2O_7 ⁻ during the reaction and unaffected by variations in the initial concentration. Addition of $Cr(ClO_4)_3$ in amounts comparable to those formed during the reaction were also found to be without effect on the rate. A small induction period was noted at the commencement of most of the reactions, before the final zero-order rate was attained. This may be an apparent effect resulting from the uncertainty in the zero reaction time, mentioned earlier, or it may be due to the presence in the solution of a trace amount of an impurity which reduces preferentially to Cr_2O_7 ⁻. For example, it is estimated that less than 10^{-5} M ClO_3 – could account for the observed effect.

It may be concluded that $Cr_2O_7^-$ does not participate directly in the rate-determining step of the reaction although, as shown earlier, ^{1c, 1d} its reduction serves as a convenient measure of the rate of activation of H₂ in the solution. Therefore, it was considered more appropriate to express the results in terms of the equivalent rate of reaction of H₂



Fig. 1.—Typical rate plots for the reduction of Cr_2O_7 by H₂; 0.1 *M* AgClO₄; 0.5 *M* HClO₄; 50°; 0.83 atm. H₂.

per liter of solution, $-d[H_2]/dt$, based on the stoichiometric equivalence of the reaction, *i.e.*

$$\frac{-\mathrm{d}[\mathrm{H}_2]}{\mathrm{d}t} = -3 \frac{\mathrm{d}[\mathrm{Cr}_2\mathrm{O}_7^-]}{\mathrm{d}t}$$
(2)

Values of $-d[H_2]/dt$ were calculated from the measured zero-order rate of disappearance of $Cr_2O_7^-$ and were generally reproducible to within $\pm 5\%$.

Evidence for the absence of any interaction, such as complex formation, between Ag^+ and $Cr_2O_7^-$ in solution, is provided by the observation that the absorption spectrum of $Cr_2O_7^-$ is unaffected by addition of Ag^+ .

The suggestion that $Cr_2O_7^{-}$ does not take part in the rate-determining step, receives support from the result of an experiment (see Table I) in which Ce^{++++} was substituted for $Cr_2O_7^{-}$ as the reaction label. Within the experimental error involved in the comparison, the rate of reaction of H₂, calculated from the zero-order rate of reduction of Ce^{++++} , was the same as that determined using $Cr_2O_7^{-}$.

Evidence for the homogeneous character of the reaction is provided by the results of another experiment (see Table I) in which the reaction vessel was packed with 2.2 g. of Pyrex glass wool. The rate was the same as in an unpacked vessel.

Figure 2 shows the rate of reaction to be directly proportional to the partial pressure of hydrogen. Since the solubility of hydrogen in water obeys Henry's law in the region under consideration,⁷ it may also be concluded that the rate is proportional to the solution concentration of hydrogen, [H₂]. Variation of the H₂ flow rate in the system, between 0.09 and 0.35 l./min., did not affect the rate, indi-

(7) H. A. Pray, C. E. Schweickert and B. H. Minnich, Ind. Eng. Chem., 44, 1146 (1952).

⁽⁶⁾ For convenience, and in accordance with common usage, the formula Cr_2O_7 is employed in this paper to denote all the Cr(VI) in the solution. It is probable, however, that at the high acidities used, other forms of Cr(VI), especially $HCrO_4^-$ and H_2CrO_4 , are present and may, in fact, predominate. Since Cr(VI) is used in this system only as a label to measure the amount of H_2 reacted, its exact form is not of importance. This shifting equilibrium does not affect the validity of the spectrophotometric analysis since the optical density of Cr(VI) was calibrated experimentally for each acidity.

Temp., °C.	Reactant M	HClO ₄ , M	NaClO ₄ . M	$k \times 10^3$,
49 6	1 67 × 10-4 K.C.	0.10	0.00	1.* mole ** se
40.6	$1.07 \times 10^{-1} \text{K}_2 \text{O}_2 \text{O}_7$	0.10	0.90	7.95
49.0	$1.07 \times 10^{-1} \text{K}_2 \text{Cr}_2 \text{Cr}_7$.20	.80	7.82
49.6	$1.67 \times 10^{-4} \text{ K}_2 \text{ Cr}_2 \text{ U}_7$. 50	. 50	8.07
49.6	$1.67 \times 10^{-4} \text{ K}_2 \text{Cr}_2 \text{O}_7$.75	. 25	8.05
49.6	$1.67 \times 10^{-4} \text{ K}_2 \text{Cr}_2 \text{O}_7$	1.00	.00	8.68
49.6	$1.67 imes 10^{-4} m K_2 Cr_2 O_7$	1.00	.00	8.36
49.6	$1.67 \times 10^{-4} \mathrm{K_2Cr_2O_7}$	1.29	.00	8.38
49.6	$1.67 \times 10^{-4} \mathrm{K_2Cr_2O_7}$	0.50	.00	8.22
49.6	$1.67 \times 10^{-4} \mathrm{K_2Cr_2O_7}$. 50	. 50	7.97
49.6	$1.67 \times 10^{-4} \text{ K}_2 \text{Cr}_2 \text{O}_7$. 50	1.00	7.77
49.6	$1.67 \times 10^{-4} \text{ K}_2 \text{Cr}_2 \text{O}_7$. 50	1.50	7.35
49.6	$1.67 \times 10^{-4} \mathrm{K_2 Cr_2 O_7}$. 50	2.00	6.67
49.6	$1.67 \times 10^{-4} \mathrm{K_2Cr_2O_7}$. 50	0.00	8.25
49.6	$1.67 \times 10^{-4} \text{ K}_2 \text{Cr}_2 \text{O}_7$. 50	.00	8.05
50.0	$0.67 \times 10^{-4} \text{ K}_2 \text{Cr}_2 \text{O}_7$. 50	.00	8.07
50.0	$1.00 imes 10^{-4} m K_2 Cr_2 O_7$. 50	.00	8.20
50.0	$1.33 imes 10^{-4}{ m K_2Cr_2O_7}$.50	.00	8.07
50.0	$1.20 \times 10^{-4} \operatorname{Ce}(\mathrm{ClO}_4)_4$. 50	.00	7.82
30.0	$1.67 imes 10^{-4} m K_2 Cr_2 O_7$. 50	.00	1.69
40.0	$1.67 imes 10^{-4} m K_2 Cr_2 O_7$. 50	.00	3.78
50.0	$1.67 imes 10^{-4} m K_2 Cr_2 O_7$. 50	.00	8.23
60.0	$1.67 \times 10^{-4} \text{ K}_2 \text{Cr}_2 \text{O}_7$, 50	.00	17.6
70.0	$1.67 \times 10^{-4} \text{ K}_2 \text{Cr}_2 \text{O}_7$. 50	.00	35.9

TABLE I

^a Reaction vessel packed with 2.2 g. of Pyrex glass wool.

cating that the latter is not limited, under the experimental conditions used, by absorption of the gas. Other aspects of the kinetics also bear this out.



Fig. 2.—Dependence of the rate on H₂ partial pressure; 0.1 M AgClO₄; 0.5 M HClO₄; 49.6°.

The catalytic influence of Ag^+ on the reaction is clearly demonstrated in Fig. 3 which shows rate plots for the reduction of $Cr_2O_7^-$ by H_2 in solutions containing various amounts of AgClO₄. No reaction could be detected in the absence of Ag^+ , while progressively higher rates were obtained as the Ag^+ concentration was increased up to 0.108

		1. ² mole ⁻² sec.
0.10	0.90	7.93
.20	. 80	7.82
. 50	. 50	8.07
.75	. 25	8.05
1.00	.00	8.68
1.00	.00	8.36
1. 2 9	.00	8.38
0.50	.00	8.22
. 50	. 50	7.97
. 50	1.00	7.77
. 50	1.50	7.35
.50	2.00	6.67
. 50	0.00	8.25
. 50	.00	8.054
. 50	.00	8.07
. 50	.00	8.20
.50	.00	8.07
. 50	.00	7.82
. 50	. 00	1.69
. 50	.00	3.78
. 50	.00	8.23
. 50	.00	17.6
. 50	.00	35.9

M. The nature of the dependence is quantitatively depicted in Fig. 4, where the reaction rates, determined at 40, 50 and 70°, are plotted as func-





tions of the concentration and square of the concentration of Ag+. At each temperature it is observed that the results conform closely to a secondorder dependence, the rate being essentially proportional to $[Ag^+]^2$. Detailed inspection reveals only a slight deviation from this relation in the direction of lower order, reflected in the fact that the linear plots of rate against $[Ag^+]^2$ do not quite extrapolate to the origin, although the uncatalyzed rate is found experimentally to be negligible; the possible significance of this will be discussed later.

Similar results, also shown in Fig. 4, were obtained when nitrate was substituted for perchlorate. The slope of the plot of rate vs. $[AgNO_3]^2$ (for solutions containing 0.5 *M* HNO₃) is about 10% lower than that for comparable perchlorate solutions, possibly the result of some complexing between Ag⁺ and NO₃⁻⁻ or the influence of a small salt effect on the reaction or on the solubility of H₂.

The results listed in Table I show that essentially no effect on the rate was observed when the HClO₄ concentration was varied between 0.1 and 1.0 M(the total ionic strength being held constant at 1.1 by simultaneous variation of the NaClO₄ concentration). Also a negligible effect was observed when the NaClO₄ concentration was varied between zero and 1.0 M in the presence of constant concentrations of 0.1 M AgClO₄ and 0.5 M HClO₄. At higher NaClO₄ concentrations (1.5-2 M) a slight decrease in the rate was noted. Unfortunately no measurements of salt effect could be made in solutions of much lower total ionic strength (*i.e.* <0.1) because of the need to maintain critical minimum concentrations of both AgClO4 and HClO4 in the solution in order to obtain measurable reaction rates and to prevent the precipitation of the slightly soluble silver dichromate.

Rates were measured at five temperatures ranging from 30 to 70°, and are listed in Table I. The results conform to a good Arrhenius plot from whose slope an apparent activation energy of 15.8 ± 0.5 kcal./mole was calculated.

Discussion

The kinetic results may be summarized in the relations

$$-d [H_2]/dt = k[Ag^+]^2[H_2]$$
(3)

$$= k[\mathrm{Ag}^+]^2 \alpha P_{\mathrm{H}_2} \tag{4}$$

where α is Henry's constant, denoting the solubility of H₂ and P_{H2} is the measured H₂ partial pressure.

The experimental data yield the following expression for the rate constant

$$k = 4 \times 10^8 \text{ exp.} \left[\frac{-15,800}{RT} \right] \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$$
 (5)

Values of k were calculated from equation 4, using Wiebe and Gaddy's values⁸ of solubility of H_2 in water.

These kinetics suggest that the rate-determining step of the reaction, in which the hydrogen apparently is activated, is a termolecular process involving the interaction of one H_2 molecule with two Ag^+ ions. The product of this combination then reacts rapidly with $Cr_2O_7^-$ to reduce the latter and yield the observed reaction products. This sequence of steps may be represented as

$$H_2 + 2Ag^+ \xrightarrow{k} (Ag_2 \dots H_2)^{++} \qquad (6)$$





followed by

The stoichiometry and kinetics of the over-all process correspond to those observed.

The detailed nature of the product of the rate-determining step is not resolved. It is possible that a stable intermediate complex (such as that depicted in equation 6) is formed, which carries the hydrogen in active form, and which proceeds to react with $Cr_2O_7^-$ before it can rearrange to form more stable products. Alternatively it is possible that Ag^+ itself is reduced homogeneously, to free Ag atoms or Ag₂ molecules, in the rate-determining step, *i.e.*

$$H_2 + 2Ag^+ \longrightarrow 2Ag^0 + 2H^+$$
 (8)

$$H_2 + 2Ag^+ \longrightarrow Ag_2 + 2H^+$$
 (9)

followed by rapid reaction of the dissolved Ag or Ag_2 with $Cr_2O_7^{-}$, so that no metallic silver is formed until after all the $Cr_2O_7^-$ is reduced. Neglecting stabilization of the uncharged Ag or Ag₂ by solvation, the endothermicities of reactions (8) and (9)are estimated, from thermochemical data⁹ and the recently determined dissociation energy of Ag_{z} ,¹⁰ to be 87.6 and 46.2 kcal./mole, respectively, both considerably in excess of the observed activation energy. It is unlikely that the difference could be accounted for by simple solvation of the Ag or Ag_{a} and consequently the earlier suggestion, involving the formation of an intermediate complex (Ag₂. H_2)⁺⁺ (or 2(Ag . . H)⁺) in which additional stabilization energy is derived through some form of electron sharing between the Ag and H atoms, is favored. Providing the intermediate reacts rapidly with $Cr_2O_7^-$, these various alternatives cannot be distinguished kinetically.

The observed frequency factor of the reaction, $4 \times 10^8 \, l^2 \, mole^{-2} \, sec.^{-1}$, corresponds to an entropy of activation ΔS_{\pm}^{+} , at 50°, of $-22 \, e.u.$ Unfortunately few data are available for other termolecular reactions on which to base a comparison of these values,

(9) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solution," Prentice-Hall, Inc., New York, N. Y., 1952.

(10) B. Kleman and S. Lindkvist, Arkiv Fys., 9, 385 (1955).

⁽⁸⁾ R. Wiebe and V. L. Gaddy, J. Am. Chem. Soc., 56, 76 (1934).

but approximate calculations,¹¹ based on collision theory, lead to an expected value of $10^{9}-10^{10}$ l.² $mole^{-2}$ sec.⁻¹ for the frequency factor of a simple gas-phase termolecular reaction. While this is of the same order as the observed value and thus provides some indication of the plausibility of the proposed mechanism, the agreement should be interpreted with caution in view of the uncertainties involved in the calculation and comparison.

A possible alternative to a termolecular rate-determining step, consistent with the observed thirdorder kinetics, would be a bimolecular step in which an intermediate binary complex, Ag_2^{++} or AgH_2^{++} (in equilibrium with its components), reacts with an H_2 molecule or Ag^+ ion, respectively, to give, in common with the earlier mechanism, a ternary activated complex containing two Ag⁺ ions and one H_2 molecule. Two such possible schemes are

Scheme A:

$$2Ag^{+} \xrightarrow{k_{1}}_{k_{2}} (Ag_{2})^{++} \text{ (fast)}$$
(10a)

$$(Ag_2)^{++} + H_2 \xrightarrow{k_3} (Ag_2 . . H_2)^{++} (slow) (10b)$$

Scheme B:

$$Ag^+ + H_2 \xrightarrow{\kappa_1} (Ag_..H_2)^+$$
 (fast) (11a)

$$(Ag..H_2)^+ + Ag^+ \xrightarrow{k_2} k_3 (Ag_2..H_2)^{++} (slow)$$
 (11b)

In either of the above cases, unless the steadystate concentration of the intermediate binary complex is fairly high, these alternatives are not readily distinguishable kinetically from a single termolecular step and are not intrinsically more probable.12 In the absence of any other evidence for the formation of such intermediates, there would appear to be no reason to favor these mechanisms over the simple termolecular mechanism proposed earlier.

The essential independence of the rate, within fairly wide limits, of the H^+ and ClO_4^- concentrations provides some support for the conclusion that the observed catalytic activity is associated with simple Ag^+ ions, rather than with OH^- or $ClO_4^$ complexes, whose concentrations in these solutions are probably very small. Apart from this, the apparent absence of a salt effect on varying the Na- ClO_4 concentration from zero to 1.0 M (in the presence of 0.1 M AgClO₄ and 0.5 M HClO₄) is inconclusive and throws little light on the reaction mechanism, since these measurements refer to a concentration region in which the activity coefficients of most electrolytes remain nearly constant with varying ionic strength.¹³ In more dilute solutions, an increase in rate with increasing ionic strength would be predicted on the basis of the Debye-Hückel theory, since the proposed mechanism involves the combination of two ions of like charge in the ratedetermining step. Unfortunately it was not possible, for the experimental reasons mentioned earlier, to make any measurements in the region ($\mu < 0.05$) where these considerations might be expected to apply.

(12) Ref. 11, p. 181.

A commonly noted tendency¹³ for the activity coefficients of many electrolytes, particularly salts of polyvalent cations (which the activated complex would approximate), to increase at very high ionic strength, may account for the observed slight decrease in rate when the NaClO₄ concentration was increased above 1 M. A salting out of H_2 under these conditions might also contribute to a decreased rate.

In some respects the present results resemble those obtained earlier for the activation of H_2 in aqueous solution by Cu^{++} and Hg^{++} salts.^{1,2} An important difference is that with the latter ions, the reactions are of first order with respect to the catalyst, only one Cu⁺⁺ or Hg⁺⁺ ion apparently being required to activate each H₂ molecule. It has been suggested¹⁴ that the catalytic activity of these ions is associated with their electron-accepting properties and that the activation process involves a transfer or partial transfer of electrons from H₂ to the catalyst. The present results are not inconsistent with this view but suggest the modification that the most favored path of activation of H₂ is apparently by simultaneous transfer of both its electrons. This would explain the fact that two Ag⁺ ions are required simultaneously to activate an H₂ molecule in aqueous solution while only one Cu^{++} or Hg⁺⁺ ion, each with a fairly high affinity for two electrons, suffices.

It is of interest that similar kinetics, *i.e.*, of second order in the catalyst concentration, were obtained for the activation of H_2 in quinoline solution by another univalent metal salt, CuOAc.¹⁵ This was originally taken as indicating that H_2 was activated by interaction with the dimeric molecule Cu₂(OAc)₅ but recently Calvin and Wilmarth,¹⁶ on the basis of a careful re-examination of this system, have proposed a termolecular rate-determining step in which H_2 is activated by simultaneous interaction with two CuOAc molecules. The striking parallel between this system and the present one, is readily evident.

Although the kinetic results leave little doubt that the most favorable path of activation of H_{ϵ} in aqueous solutions of Ag⁺ salts is by interaction with two Ag+ ions, the small deviation from the exact proportionality between the rate and $[Ag^+]^2$ in the direction of a lower order of dependence, mentioned earlier, suggests that an alternative catalytic path, involving only one Ag+ ion, may also be possible although less favorable. The relative contribution of the reaction proceeding by such a path should become more pronounced at lower Ag⁺ concentrations, but unfortunately the technique used in the present study precluded any measurements in the region below $0.02 M \text{ Ag}^+$ because of the slow rates involved. It is hoped to extend the investigation to this region in the future by using a modified technique. This question is of particular interest in view of recent work⁵ on the

⁽¹¹⁾ A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons Inc., New York, N. Y., 1953, p. 72.

⁽¹³⁾ B. E. Conway, "Electrochemical Data," Elsevier Publishing Co., New York, N. Y., 1952, pp. 75-83.

⁽¹⁴⁾ J. Halpern and E. Peters, J. Chem. Phys., 23, 605 (1955).

^{(15) (}a) M. Calvin, Trans. Faraday Soc., 34, 1181 (1938); J. Am. Chem. Soc., 61, 2230 (1939); (b) S. Weller and G. A. Mills, ibid., 75, 769 (1953); (c) W. K. Wilmarth at | M. K. Barsh, ibid., 75, 2237 (1953).

⁽¹⁶⁾ M. Calvin and W. K. Wilmarth, J. Am. Chem. Soc., 78, in press (1956).

Mar., 1956

activation of H_2 by AgOAc and CuOAc in pyridine solution where (in contrast to the quinoline system) first-order rates in the catalyst concentration were observed. Acknowledgment.—Support of this work through a grant and a Fellowship award to one of the authors (A.H.W.) from Canadian Industries, Ltd., is gratefully acknowledged.

KINETICS OF THE REACTION OF MOLECULAR HYDROGEN WITH MERCURIC AND MERCUROUS PERCHLORATES IN AQUEOUS SOLUTION

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The kinetics of the reduction of Hg^{++} and Hg_2^{++} by molecular hydrogen in aqueous perchlorate solution have been examined. The results are shown to be consistent with a mechanism in which H_2 is activated initially by homogeneous interaction with either Hg^{++} or Hg_2^{++} , in the rate-determining step. The final products are determined by thermodynamic considerations. The total rate of reaction of H_2 is given by $(k_1[Hg^{++}] + k_2[Hg_2^{++}])[H_2]$, where $k_1 = 4.2 \times 10^{10} \exp[-18,100/RT]$ and $k_2 = 1.2 \times 10^{11} \exp[-20,400/RT]$ liter mole⁻¹ sec.⁻¹, respectively. Possible mechanisms of the activation process are discussed.

Introduction

A preliminary study of the reduction of mercuric acetate by molecular hydrogen in aqueous solution, was described in an earlier paper.¹ The bimolecular kinetics suggest that H_2 is activated homogeneously by interaction with $Hg(OAc)_2$, or other mercuric acetate complexes, in the rate-determining step. However, detailed interpretation of the kinetics was difficult because of uncertainties relating to the extent of complexing between Hg^{++} and OAc^- and to the possible influence, on the reaction, of the mercurous acetate product. Hence it seemed desirable to undertake a similar study using perchlorate solutions, in which cations such as Hg^{++} and Hg_2^{++} are believed to be essentially uncomplexed. During the course of this investigation it proved necessary also to resolve the kinetics of the reaction of Hg_2^{++} with H_2 .

The work which is described in this paper forms part of a series of recent investigations, conducted in this Laboratory, on the homogeneous catalytic activation of molecular hydrogen in aqueous solution by metal ions. Related studies on cupric² and silver³ salts have been described earlier but, apart from the preliminary investigation on Hg- $(OAc)_2$, no previous kinetic work on the present system appears to have been reported.

Experimental

All chemicals employed were of Reagent grade. IIg-(ClO₄)₂ and NaClO₄ were obtained from G. F. Smith Chemical Company. Other reagents were Baker and Adamson products. The solutions used in the kinetic experiments were prepared by diluting standardized stock solutions with distilled water. H₂ and N₂ gases were obtained from Canadian Liquid Air Company. The solutions were one water for Hr. $\pm \pm$ by notantiomat-

The solutions were analyzed for Hg_2^{++} by potentiometric titration with KMnO₄. The total Hg concentration was determined by titration with KCNS using a ferric indicator, following oxidation with KMnO₄. The concentration of Hg⁺⁺, estimated from the difference between these two

(1) J. Halpern, G. J. Korinek and E. Peters, *Research (London)*, 7, S 61 (1954).

(2) (a) J. Halpern and R. G. Dakers, J. Chem. Phys., 22, 1272
(1954); (b) R. G. Dakers and J. Halpern, Can. J. Chem., 32, 969
(1954); (c) E. Peters and J. Halpern, *ibid.*, 33, 356 (1955); (d) E. Peters and J. Halpern, THIS JOURNAL, 59, 793 (1955).

(3) A. H. Webster and J. Halpern, ibid., 60, 280 (1956).

values, always agreed well with that determined directly by the cyanide method.⁴

The kinetic experiments were made in a cylindrical autoclave similar to that described earlier.²⁹ It was constructed entirely of 316 stainless steel which proved inert to all the solutions used and without effect on the reaction. The inside dimensions of the vessel were about 6 in. diameter by 9 in. height. A stirrer shaft, thermometer well, thermoregulator well and sampling tube, extending below the surface of the solution, were connected through the lid. The solution was stirred with an impeller of 3 in. diameter which was generally rotated at 970 r.p.m. The partial pressure of H₂ was controlled by a standard gas regulator. The autoclave was heated externally with a gas burner, connected through a solenoid valve which was actuated by an electronic relay. Using a mercury thermoregulator the temperature of the solution could be controlled to within $\pm 0.1^\circ$. Four liters of solution, of desired composition, was placed

Four liters of solution, of desired composition, was placed in the autoclave which was then sealed, flushed with nitrogen and heated to the reaction temperature. The solution was allowed to remain at temperature under nitrogen, usually for about 30 minutes, during which it was sampled and analyzed to ascertain its stability in the absence of hydrogen. The nitrogen was then discharged and hydrogen was introduced and maintained throughout the experiment at a constant partial pressure. Zero reaction time, recorded at the instant of introduction of the hydrogen, may be subject to an uncertainty of up to a few minutes because of the time required for the solutions to become saturated. During the course of the reaction, the solution was sampled periodically and analyzed as described earlier.

Results and Discussion

The results of a typical rate experiment are depicted in Fig. 1. No change in solution composition occurred in the absence of hydrogen. The reaction in the presence of hydrogen can best be described in terms of two clearly defined stages. Stage A corresponds to the reduction of Hg⁺⁺ to Hg₂⁺⁺ according to the stoichiometric equation

$$2Hg^{++} + H_2 \longrightarrow Hg_2^{++} + 2H^+ \qquad (1)$$

It is characterized by a progressive decrease in the mercuric ion concentration, $[Hg^{++}]$, and an equivalent increase in the mercurous ion concentration, $[Hg_2^{++}]$, the total concentration of dissolved Hg remaining constant. This stage persists until about 99% of the Hg^{++} has been reduced to Hg_2^{++}.

During the following stage, B, the remaining Hg^{++} , and the Hg_2^{++} formed in the first stage, are

(4) I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1947, p. 197.