TABLE V (*Continued*)

y	$f(y)$	y	$f(y)$
.12	.0975	14	.939
.14	.1121	16	.947
.16	.1264	18	.952
.18	.1402	20	.957
.20	.1537	25	.966
.25	.186	30	.971
.30	.216	40	.978
.35	.244	50	.982
.40	.271	100	.991
.45	.296	200	.996
.50	.319	500	.998
.60	.362	1000	.999
.70	.400		

since, regardless of any interpretation of the reverse process, the region of total irreversibility definitely indicates a slow step in the reduction process. This is further supported by the observation that altering the effective stream length had no pronounced effect on the observed constants in Table IV. The poorest agreement for a threefold change in stream length was found in the case of the 0.9 *M* KCl solution, where the rate constant varied from about 0.8×10^{-2} to 1.1×10^{-2} cm./sec. This is in contrast to the very pronounced effect on the reaction rate of altering the concentration of inert electrolyte.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Kinetic Study of the Reduction of Chromium(VI) at Rotating Gold Microelectrodes

BY FREDERICK BAUMANN[1] AND IRVING SHAIN

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The kinetics of the reduction of chromium(VI) at a rotating gold microelectrode were investigated. Equations were developed which permit the calculation of the rate of the electrode reaction from current-voltage curves, using solid electrodes in stirred solution. Over the range of hydrogen ion concentrations studied, the activated complex for this electrode reaction was found to have the composition $H_3CrO_4^x$, where x is the charge. A possible mechanism is postulated.

The reduction of chromium(VI) species at the dropping mercury electrode has been reported many times.[2-4] All of these studies were made in basic or weakly acidic solutions. The extension of these studies to lower *p*H values has not been possible because the rising portion of the current–voltage curve is shifted more positive than the anodic dissolution potential of mercury. It has not been possible to obtain a reduction wave for chromium(VI) on platinum electrodes since chromium(VI) in acid solution attacks platinum and the oxide film formed hinders the electrode reaction. However, gold electrodes were found suitable since they are resistant to attack by chromium(VI) species in acid solution.[5]

Although rotating solid microelectrodes have found many analytical applications, studies of the rising portion of the current–voltage curves obtained with these electrodes have not been very successful. Poor reproducibility, due to surface effects caused by oxide films and impurities, has hindered these studies. Since reproducible results can be obtained for the reduction of chromium(VI) in acid solution at rotating gold electrodes, a kinetic study was made of this reaction.

Theory

Delahay[6] has developed a unified theory of polarographic waves which rigorously treats polarographic waves regardless of the degree of irreversibility of the electrode process. This theory is applicable to the dropping mercury electrode where diffusion is the only mode of mass transfer. Using the approach of Delahay and Strassner,[7] an analogous theory for the case of electrodes of constant area in stirred solutions can be derived.

Consider the reduction of substance O to substance R in an electrode process involving n electrons, where R is soluble in the solution

$$O + ne = R$$

The current is given by

$$i = nFAf(x = 0) \qquad (1)$$

where F is the faraday, A is the area of the electrode and $f(x = 0)$ is the flux at the electrode surface. If the overvoltage is sufficiently high so that the effect of the backward reaction can be neglected, the flux can be equated to the concentration of O on the electrode surface and the rate at which it reacts. For a first-order reaction

$$f(x = 0) = kC_0 \qquad (2)$$

where C_0 is the concentration of the reactant at the electrode surface and k is the formal heterogeneous rate constant for the forward electrode reaction, expressed in centimeters/second. Combining equations 1 and 2

$$i = nFAkC_0 \qquad (3)$$

The concentration at the electrode surface can be related to the bulk concentration by[8]

$$C_0 = \frac{i_l - i}{i_l} C_0^0 \qquad (4)$$

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(1) Based on the Ph.D. thesis of Frederick Baumann, University of Wisconsin, 1956.

(2) J. J. Lingane and I. M. Kolthoff, THIS JOURNAL, **62**, 852 (1940).

(3) T. Berzins and P. Delahay, *ibid.*, **75**, 5716 (1953).

(4) J. H. Green and A. Walkley, *Australian J. Chem.*, **8**, 51 (1955).

(5) F. Baumann and I. Shain, to be published.

(6) P. Delahay, THIS JOURNAL, **75**, 1430 (1953).

(7) P. Delahay and J. E. Strassner, *ibid.*, **73**, 5219 (1951).

(8) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1952, p. 191.

where[9]

$$i_l = nFA\beta C_0^\circ \qquad (5)$$

The mass transfer coefficient β is a function of the area of the electrode and the rate of stirring. Although equation 4 originally was derived for a diffusion process, it also is applicable when convection is the mode of mass transfer. Combining equations 3, 4 and 5

$$i = nFAC_0^\circ \frac{k\beta}{k + \beta} \qquad (6)$$

This equation describes the current at any point on a current–voltage curve as a function of the rate of mass transfer and the rate of the electrode reaction, and is applicable to any electrode of constant area. Since the mass transfer coefficient is a function of the area of the electrode and of the diffusion coefficient of the reactant a different value for β must be calculated for every electrode and for every reactant.

The rate constants calculated from equation 6 are a function of potential[10]

$$k = k^\circ \exp \frac{-\alpha n_a F}{RT}(E - E^\circ) \qquad (7)$$

where k° is the formal heterogeneous rate constant for the forward electrode reaction when $E = E^\circ$, E° is the standard potential, α is the electron transfer coefficient, n_a is the number of electrons in the rate-determining step, and the other terms retain their usual significance. Equation 7 is applicable to electrode processes whose kinetics are controlled by a single rate-determining step.

Since the area of the electrode is a constant, relative values of k° may be determined by combining equations 6 and 7.

$$\log \frac{i}{i_l - i} + \log A\beta = \log Ak^\circ - \frac{\alpha n_a F}{2.3RT}(E - E^\circ) \qquad (8)$$

Thus the kinetics of a reaction at an electrode of constant area may be investigated by plotting $\log [i/(i_l - i)]$ as a function of $E - E^\circ$.

Experimental

Apparatus.—A Sargent Model XXI recording polarograph was used for the measurement of the current–voltage curves. The potential scanning rate was 2.5 mv. per second. Potentials were measured with a Rubicon portable precision potentiometer. All potentials are referred to the saturated calomel electrode (S.C.E.).

The rotating gold electrode was constructed by fitting gold wire (J. Bishop and Co. Platinum Works, 99.97% pure, 0.81 mm. diameter) into a Teflon tube. The length of the electrode was 5 mm. The electrode was rotated at exactly 1080 r.p.m. by means of a synchronous motor.

Electrolysis was carried out in a 250-ml. tall form beaker equipped with a side stem for the introduction of nitrogen. The electrolysis cell was connected to a saturated calomel electrode by means of a double junction salt bridge containing the indifferent electrolyte and saturated sodium chloride. This effectively prevented the diffusion of chloride ions into the electrolysis cell. The reference electrode and electrolysis cell were thermostated at 25 ± 0.02°. The resistance of the cell was 175 ohms. All the current–voltage curves were corrected for the *IR* drop across the cell.

Materials.—All reagents had to be of the highest purity for this kinetic study. The solutions were prepared from doubly distilled water. The second distillation was carried out from alkaline permanganate in an all-Pyrex glass system. The first 20 ml. of each batch were discarded.

The sodium perchlorate solutions were prepared from G. F. Smith hydrated sodium perchlorate. A concentrated stock solution was prepared and was analyzed by evaporating 10 ml. to constant weight at 350°. Reducible impurities in this reagent were found to interfere with the reduction of chromium(VI). Electrolysis at a mercury cathode set at −0.7 volt for 48 hours was found to remove these impurities satisfactorily.

The perchloric acid solutions were prepared from Baker and Adamson 60% reagent grade perchloric acid without further purification. Stock chromium(VI) solutions were prepared from Mallinckrodt Analytical Reagent grade potassium dichromate without further purification. Since oxygen is reduced in the potential range studied, Linde high purity nitrogen was used to deaerate the solutions.

Results

The reduction was studied by obtaining current–voltage curves at various perchloric acid concentrations and at various chromium(VI) concentrations. The acid concentrations were 0.500, 0.100 and 0.010 molar. The ionic strength was kept constant at 1.00 by the addition of appropriate amounts of sodium perchlorate. The concentrations of chromium(VI) were 1.32×10^{-6}, 6.60×10^{-6}, 5.28×10^{-5} and 1.32×10^{-4} molar.

Each current–voltage curve was analyzed using equation 8. Log Ak was calculated from values of the current along the rising portion of the wave and plotted against E. The lines obtained were straight and nearly parallel indicating that the effect of impurities has at least been made constant if not eliminated.

The fact that the lines were straight indicates that the reduction follows a first-order mechanism with respect to the reactant. If a higher order mechanism was followed, each line would be bent since the current (rate) at the foot of the wave would depend on the order of the reactant, but in the limiting current region the dependency would be first order since mass transfer is the limiting factor. The results are summarized in Table I.

The average value of αn_a obtained from the slopes of the lines was 0.95 (average deviation, 0.05). The fact that the lines are straight and that the values of αn_a are constant indicates that there is only one rate determining step throughout the concentration ranges studied. Thus the application of equation 8 is valid in this study.

TABLE I

VALUES OF αn_a AT VARIOUS CHROMIUM(VI) AND HYDROGEN ION CONCENTRATIONS

[Cr(VI)], moles/l.	[H⁺], moles/l.	E (*vs.* S.C.E.) at log Ak = −6.0	αn_a
1.32×10^{-6}	0.50	0.455	0.91
	.10	.390	.89
	.01	.275	.98
6.60×10^{-6}	.50	.458	.98
	.10	.390	1.00
	.01	.308	0.95
5.28×10^{-5}	.50	.496	1.00
	.10	.394	0.98
	.01	.321	1.00
1.32×10^{-4}	.50	.532	0.98
	.10	.396	.87
	.01	.319	.85

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(9) I. M. Kolthoff and J. Jordan, THIS JOURNAL, **76**, 3843 (1954).

(10) H. Eyring, L. Marker and T. C. Kwoh, *J. Phys. Colloid Chem.*, **53**, 187 (1949).

Effect of Hydrogen Ion.—The reduction of chromium(VI) can be considered a first-order reaction if the hydrogen ion concentration is kept constant even though hydrogen ions are involved in the rate-determining step. This condition was fulfilled experimentally since the lowest hydrogen ion concentration (0.01 molar) is considerably higher than the highest chromium(VI) concentration (1.32×10^{-4}). Under these conditions, the hydrogen ion concentration at the electrode surface is equal to the bulk concentration, and equation 8 can be modified to

$$\log AK = \log \frac{i}{i_l - i} + \log A\beta = \log AK^\circ - \frac{\alpha n_a F}{2.3\,RT}(E - E^\circ) \quad (9)$$

where the rate constants K and K° are given by

$$K = k(H^+)^b \quad (10)$$

and

$$K^0 = k^0(H^+)^b \quad (11)$$

Relative values of log AK° were obtained from the log plots described in Table I by measuring log AK at an arbitrary value of E° (0.430 volt *vs.* S.C.E.). These values are shown in Table II. The average values of log AK° at a particular hydrogen ion concentration were used to calculate the hydrogen ion dependence. The deviation of these values at a particular hydrogen ion concentration is slightly larger than the expected experimental error, but is not so large as to prevent the calculation of an integer: the hydrogen ion dependency. The deviation is probably an effect of residual impurities.

TABLE II

VALUES OF LOG AK^0 AT E = 0.430 VOLT (*vs.* S.C.E.)

		Concn. perchloric acid, moles/l.		
		0.500	0.100	0.010
Concn. Cr(VI) (moles/l.)	1.32×10^{-6}	−5.61	−6.61	−8.53
	6.60×10^{-6}	−5.53	−6.66	−7.96
	5.28×10^{-5}	−4.83	−6.60	−7.91
	1.32×10^{-4}	−4.32	−6.53	−7.65
	Av.	−5.07	−6.60	−8.01

Since the value of the limiting current is used in evaluating log AK°, b will not be an integer when calculated from equation 11 because the limiting current is proportional to the total chromium(VI) concentration rather than the predominant chromium(VI) species.

The predominant species of chromium(VI) which exist in the concentration ranges studied are $Cr_2O_7^=$, $HCr_2O_7^-$, $HCrO_4^-$ and H_2CrO_4.[11] If $HCrO_4^-$ is assumed to be the reactive species, an expression of the form

$$\text{rate} = \frac{k^\circ K_c[\text{Cr(VI)}][\text{H}^+]^p}{K_c + [\text{H}^+]} \quad (12)$$

can be derived where

$$K_c = \frac{[\text{H}^+][\text{HCrO}_4^-]}{[\text{H}_2\text{CrO}_4]} \quad (13)$$

and

$$[\text{Cr(VI)}] = [\text{H}_2\text{CrO}_4] + [\text{HCrO}_4^-] \quad (14)$$

Similar equations could have been derived assuming other reactive species. However, for the evaluation of p it is not necessary to know which species is reactive.

Using equation 12 and the Tong and King[11] value for K_c of 1.21, a plot of log AK° + log (K_c + [H^+]) *vs.* the hydrogen ion concentration allows the hydrogen ion dependency of this reaction to be evaluated (Table III).

TABLE III

HYDROGEN ION DEPENDENCY FOR THE REDUCTION OF CHROMIUM(VI)

log [H^+]	log AK° + log (K_c + [H^+])
−0.3	−4.84
−1.0	−6.48
−2.0	−7.92

The slope gives a value for p of 1.8 ± 0.3. Since a value of 2 is within the error limits and since fractional values are not possible, a second-order dependency on the hydrogen ion concentration is inferred.

The results indicate an activated complex of the composition $H_3CrO_4^x \pm nH_2O$, where x is the charge.

Discussion

Mechanism.—A knowledge of the charge of the activated complex is necessary to postulate mechanisms for this reduction. In order to determine the electron change n_a involved in the rate-determining step, a knowledge of the value of the electron transfer coefficient α is necessary. The value of α depends on the symmetry of the energy barrier along the reaction coördinate and ordinarily values of α are close to 0.5.[12]

The possible values for n_a are 1, 2 or 3 since there are three electrons involved in the reduction of chromium(VI). A value of n_a equal to 3 is improbable since this would require α to equal 0.32 and a mechanism which requires the reversible gain of two electrons before the rate-determining step. Although a value of α equal to 0.95 is consistent with a possible mechanism (a slow step involving one electron, followed by the reversible gain of two electrons), this value of α is inconsistent with the high overvoltage associated with this reaction. A value of n_a equal to two seems to be the most probable, since α is equal to 0.48 and since there is good evidence for the existence of chromium(IV) as an intermediate in other reactions involving the reduction of chromium(VI).[3,13,14]

Any mechanism which is proposed for the reduction of chromium(VI) will have to explain the formation of an activated complex containing three hydrogens. Since the final species—chromium(III)—is a cation, the negative charge acquired by the chromium(VI) species due to the gain of electrons must be neutralized along the reaction path. If the energy of activation is lowered by neutralization of the charge before the activated complex is formed, the formation of the activated complex

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(11) J. Y. Tong and E. L. King, THIS JOURNAL, **75**, 6180 (1953).

(12) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw–Hill Book Co., Inc., New York, N. Y., 1941, Chapt. X.

(13) P. Delahay and C. C. Mattax, THIS JOURNAL, **76**, 874 (1954)

(14) F. H. Westheimer, *Chem. Revs.*, **45**, 419 (1949).

will involve hydrogen ions. An analogous situation was encountered by King and Pandow[15] while studying the oxidation of bromide ion by cerium(IV). The following mechanism is postulated to explain the reduction of chromium(VI). It is based on the reactive species being $HCrO_4^-$ since it is the predominant species in these solutions. The steps are

$H^+ + HCrO_4^- = H_2CrO_4$ fast
$H_2CrO_4 + e^- = H_2CrO_4^-$ fast
$H^+ + H_2CrO_4^- = H_3CrO_4$ fast
$H_3CrO_4 + e^- = H_3CrO_4^-$ slow
$Cr(IV) = Cr(III)$ fast

Acknowledgment.—The authors wish to thank E. I. du Pont de Nemours and Co., and the Wisconsin Alumni Research Foundation for financial assistance.

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[15] E. L. King and M. L. Pandow, THIS JOURNAL, **75**, 3063 (1953).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Oxidation of Lower Paraffin Hydrocarbons. II. Observations on the Role of Ozone in the Slow Combustion of Isobutane[1]

BY CLARENCE C. SCHUBERT, S.J., AND ROBERT N. PEASE

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The reaction of ozonized oxygen (*ca.* 3-6 mole % O_3) with isobutane in the temperature range 110 to 270° was compared with the slow uncatalyzed reaction with oxygen alone. The ratio of gram atoms of oxygen fixed in liquid product to moles of ozone added increased from 3.4 at 125° to 4.2 at 200° and 5.0 at 225°. The ozone-induced oxidation merges into the normal slow combustion reaction at *ca.* 265°. Approximately one third of the condensed products of the isobutane–ozone reaction at 150° was found to be *t*-butylhydroxymethyl peroxide. The same peroxide was indicated to be a product of the isobutane–oxygen reaction at 270° by a comparison of infrared spectra. It is proposed that ozone may be the active intermediate responsible for chain branching during the slow combustion of hydrocarbons in oxygen. Ozone might result from the reaction: $RO_2\cdot + O_2 \rightarrow O_3 + RO\cdot$ Ozone probably has the stability requirements to account for the cool flame reaction and negative temperature coefficient region observed in the combustion of hydrocarbons. Preliminary attempts to detect ozone during the normal slow reaction by observing the ultraviolet absorption in a 3-meter tube were unsuccessful due to general absorption in the 2500 Å. region.

The preceding paper in this series[2] described the reaction of ozonized oxygen with paraffins at low temperatures, *i.e.*, 25–50°. This study has been extended to include the temperature range 110–270°. At the higher temperatures employed the reaction with ozonized oxygen merges into the uncatalyzed slow combustion reaction. In this paper the oxidation of isobutane in the presence of ozone and in its absence are compared, with attention paid to the identification of peroxidic products.

Recently, Batten, *et al.*,[3] have investigated in a static system the slow oxidation of isobutane, and Neu[4] has reported on the oxidation of *n*-butane. Current theories relative to the slow combustion of hydrocarbons favor the postulation of peroxides or of aldehydes as the intermediates responsible for the termination of the initial induction period and for chain branching. These theories are reviewed by Batten, *et al.*[3] It is of interest that these authors conclude that peroxides in their normal state are not the substances responsible for the termination of the first induction period. This work may aid in deciding whether ozone is a likely candidate for the role of intermediate.

Three aspects of the slow oxidation reaction were considered: (1) the formation of liquid products from the reaction of ozonized oxygen with isobutane in the temperature range 110–270°; (2) the reaction without added ozone at *ca.* 270°; (3) the identification of the peroxidic material formed in the isobutane–ozone and the isobutane–oxygen reaction.

Experimental Method

Isobutane (C.P. grade from Matheson Co.) was mixed with varying amounts of ozonized oxygen, then passed through a heated glass reactor in a flow system. Condensible products were collected in a trap kept at 0° and weighed. The rate of production of this liquid condensate was taken as a rough measure of the extent of reaction. The reactor was a 5-cm. Pyrex cylinder of 640-ml. volume. Prior to initial use it was cleansed with hot concentrated nitric acid followed by rinses with distilled water and a final rinse with a saturated solution of boric acid. The reactor was mounted in a vertical position in a furnace; the reactant gases without preheating entered at the top and products emerged at the bottom where they were collected in a trap immersed in ice-water. Temperatures were measured by means of a thermometer placed in contact with the reaction vessel. Due to the exothermic nature of the reaction and the impossibility of preheating the ozone more rigid temperature control was precluded.

Commercial tank oxygen was ozonized by means of a Siemens type ozonizer constructed of Pyrex and provided with a grounded condenser jacket filled with circulating cooling water. Ozonized oxygen was mixed with isobutane in a 2 mm. capillary tube, then introduced directly into the reactor by a 5-cm. length of this same 2 mm. capillary. Ozone concentrations were measured by an infrared absorption method calibrated, in turn, by an absolute method similar to that described by Jahn[5] (decomposition at a heated platinum filament).

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[1] Taken from a thesis submitted by C. C. Schubert S.J. in partial fulfillment of the requirements for the Ph.D. degree. The work described in this paper was jointly supported by Contract NOrd-7920 with the U. S. Naval Bureau of Ordnance as coördinated by the Applied Physics Laboratory, The Johns Hopkins University; and by Contract N6-ori-105 with the Office of Naval Research as coördinated by Project Squid, Princeton University. Reproduction, translation, publication, use and disposal in whole or in part by or for the United States Government is permitted.

[2] C. C. Schubert S.J. and R. N. Pease, THIS JOURNAL, **78**, 2044 (1956).

[3] J. J. Batten, H. Gardner and M. Ridge, *J. Chem. Soc., London*, 3029 (1955); J. J. Batten and M. Ridge, *Australian J. Chem.*, **8**, 370 (1955).

[4] J. T. Neu, Abstracts 127th ACS Meeting, April 1955, paper No. 50, p. 16P. Also, *J. Phys. Chem.*, **60**, 320 (1956).

[5] S. Jahn, *Ber.*, **43**, 2319 (1910).