cording alpha-counter and the concentration of protactinium in the two specimens of terrestrial and of meteoritic material calculated.

From these data and the corresponding radium concentrations of the same specimens determined independently, the weight ratios Pa/Ra have been derived for the two materials. From these results the conclusion has been reached that within the limits of error the age of the uranium atoms in this specimen of the Pultusk meteorite is the same as for terrestrial uranium.

The method is capable of estimating as little as 10^{-13} g. of Pa per g. of siliceous material, and the limit may probably be lower than this if larger samples are taken.

Rates of the Thermal Reduction of Dichromic Acid by Quinine, Hydroquinine, and Cinchonine in Dilute Sulfuric Acid at 0 to 60°

BY LAWRENCE J. HEIDT

Quinine and ten similar alkaloids reduce dichromic acid when ultraviolet light is absorbed by the alkaloid.[1] This reaction was studied in dilute sulfuric acid at 0 to 30°. The variations in the photochemical efficiencies with structural changes in the alkaloids suggested that the hexavalent chromium was reduced mostly by the secondary hydroxyl group.[1d] The kinetics of the photochemical reaction were also studied and interpreted.[1c] This paper presents a study of the kinetics of the thermal reaction in the same environment.

Materials.—The source and purification of the reagents were the same as in the photochemical work. Acid solutions were standardized by comparison with sample 84 of U. S. Bureau of Standards potassium acid phthalate.

Stock solutions of ferrous ammonium sulfate were made from clear green crystals of Analytical Reagent material and were stored in the dark. They were standardized against dichromate solutions each week they were used and the proper factors at other times interpolated.

Apparatus and Procedure.—One of the two reaction cells is sketched[2] in Fig. 1a. The stirrer was the Pyrex plunger, D. In the cell not sketched, the part of D containing the disks was replaced with a Pyrex ribbon twisted like a screw. The fall of each plunger was cushioned by a Pyrex button fused onto the end that struck the bottom of the cell. An iron nail, B, was sealed into the top of each plunger whereby it was lifted at intervals by an electromagnet and fell when a "flasher" interrupted the current in the magnet. The cell outlet, C, used in the preliminary work, was replaced by a glass joint whose cap contained the male part made of solid glass. An umbrella fused

to this cap fit loosely around the joint and extended as far down as the female part illustrated in the sketch. The volume of each cell was 100 cc. Their other characteristics have been published,[3] although these cells and the accompanying apparatus were used first in this research.
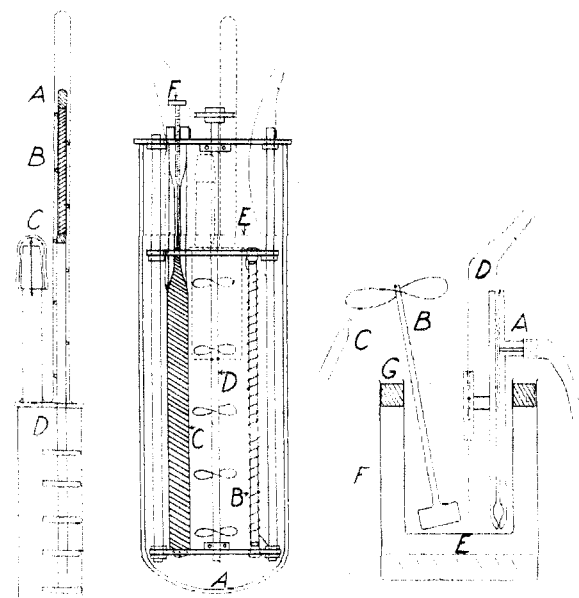

Fig. 1a.   Fig. 1b.   Fig. 1c.

The arrangement of the apparatus in the thermostat is sketched in Fig. 1b. The thermoregulator was a relay operated by a vacuum tube whose grid was in series with the contact, F, made in the glass capillary. This capillary was sealed to a welded steel tube filled with mercury. The quick response of the mercury in the steel tube to changes in the temperature of the bath enabled all adjustments for a new temperature setting to be completed within an hour. The bath then remained within 0.01° for ten hours and within 0.03° for several days. The container was the silvered dewar flask, A. The level of the thermo-

(1) (a) Luther and Forbes, THIS JOURNAL, **31**, 770 (1909); (b) Forbes, Heidt and Boissonas, *ibid.*, **54**, 960 (1932); (c) Forbes, Heidt and Brackett, *ibid.*, **55**, 588 (1933); (d) Forbes and Heidt, *ibid.*, **55**, 2407 (1933); (e) Heidt and Forbes, *ibid.*, **55**, 2701 (1933); and (f) Forbes, *Cold Spring Harbor Symposia Quant. Biol.*, **2**, 1 (1935).

(2) Mr. Arnold J. Levine made the drawings in Fig. 1, with financial aid from the National Youth Administration.

(3) Heidt and Purves, THIS JOURNAL, **60**, 1206 (1938).

stating oil was kept at E. In later work above 60° it became necessary to place the glass capillary outside of A, and connection with the steel tube was made through a piece of steel capillary. The contact with the grid was then made at room temperature—held within 2° to maintain the bath within the ranges of temperature given above.

At 0°, the reaction vessels were placed in a mush of crushed ice and distilled water in a commercial one-gallon (5-liter) vacuum jug fitted with a light-proof cover but without any other apparatus to control the temperature. Nevertheless, T remained at 0.00° in the center of the bath around the reaction cell. Only clear pieces of ice were used and they were washed with distilled water. Stirring of the reacting mixtures was restricted to shaking the cell and contents just before removing a sample, and weighing it out directly for analysis.

Reference (3) describes the way in which temperatures were measured and solutions brought quickly to the temperature of the thermostat. Tared samples of dry alkaloid and stock solutions of sulfuric acid and potassium dichromate were used to make up the reaction mixtures. When less than 10 mg. of alkaloid was required, the appropriate volume of a more concentrated, *freshly prepared* solution was used. This procedure helped avoid any peroxide which might have formed if stock solutions of these alkaloids had been kept in contact with air for long periods.

Reactions were followed by measuring the change in concentration of the substances that oxidized, in acid solution at room temperature, solutions of ferrous ammonium sulfate. Presumably these oxidizing substances were mainly hexavalent chromium, so the measured rate has been taken as $-\Delta(K_2Cr_2O_7)/\Delta t$.

The apparatus sketched in Fig. 1c was used to titrate the weighed samples of the reaction mixtures. These were placed in the inner beaker, E, and thermostated with a water-bath in the outer beaker, F, centered with the cork ring, G. The end-point was taken as the maximum potential difference, p. d., produced between the platinum wires, D, by a drop of titer. This maximum usually occurred within five drops (0.1 ml.) after the bulb (volume about 0.02 ml.) surrounding one of the electrodes had been flushed by blowing repeatedly through A until no p. d. between the electrodes dipping in the solution was measurable. The galvanometer which detected the p. d. had a sensitivity of 45 meg., and a CDRX of 18,000 ohms. Analyses were reproduced to 0.03 g. of 0.001 M Mohr salt. Solutions were weighed to 1 mg., and were transferred with clean, dry pipets.

Samples for analyses were taken from tubes at 0° or directly from the reaction cell if at 0°. The tubes were sealed with glass caps ground to fit tightly without grease. Often, two sets of analyses were made upon the samples in the tubes; the first set, within an hour after the sample had been transferred from the reaction cell, and the second set, after the sample had stood overnight at 0°. The difference between the two sets was usually small, so that a linear extrapolation was made to the time when the sample was taken from the reaction cell. When the correction thereby applied to the first set of analyses was less than 0.2%, the second set was omitted for the remaining samples.

The photochemical reaction was made negligible by keeping the reacting solutions in the dark except during sampling and when made up and analyzed in dim, diffuse light.

Results

The initial concentration of the sulfuric acid was fixed at 1.55 M, so that only a small fraction of the hydrogen ions was consumed. The pH, therefore, remained almost unchanged throughout the reaction. The thermal as well as the photochemical reactions were paralyzed even at 60° in the absence of added acid, and a precipitate appeared when the alkaloid and dichromate concentrations were much greater than 0.0003 M.

The increase in the initial rate of the reaction with the concentrations of dichromate and alkaloid are plotted on a logarithmic scale in Figs. 2A and 2B. The abscissa has been adjusted to make the points at 0, 30 and 60° coincide at 0.000167 M dichromate and 0.01 M alkaloid. The reaction rates were the same in either cell, and each point on the plot represents the average of many experiments, which agreed within 5% in the stirred solutions and within 10% in solutions not stirred. The rates for quinine, hydroquinine, and cinchonine were the same within the limits of error.

The straight lines through the points in Figs. 2A and 2B are given by equation (1) $-\Delta(K_2Cr_2O_7)/\Delta t = k(K_2Cr_2O_7)(alkaloid)^{1/2}$. The average k in kilograms$^{1/2}$ moles$^{-1/2}$ and minutes^{-1} was 0.00055 at 0°, 0.0026 at 30°, and 0.011 at 60°.

The straight line through the points on the plot, in Fig. 2C, of $\log_{10} k$ against $1/T$, is given by equation (2) $\log_{10} k = 4.05 - 2000/T$. $T = 273.2° + °C$. The energy of activation is 9 kilocalories.

In quinine, the methoxyl group in position six of the quinoline nucleus, and the vinyl group, do not enter the reaction; otherwise, equation (1) would not be expected to hold for all three alkaloids unless the rates of oxidation of these groups were also given by (1). The small activation energy suggests that a large number of degrees of freedom contribute energy to the activation process in accord with the large conjugated system of single and double bonds which transmit energy readily throughout the quinoline part of the alkaloid. It may also mean that the potential of the oxidation–reduction system and the steric factor largely determine these rates. The small value of the frequency factor implies a large steric effect often associated with reactions between complex molecules.[4]

(4) See, for example, H. W. Melville, *Chem. Soc., Annual Reports*, **35**, 69 (1939).

As the thermal reaction proceeded, its rate at first increased slightly as shown, for example, at 30° in Table I, before it began to decrease very slowly as the hexavalent chromium continued to disappear.

TABLE I

Temp., 30.0°; quinine, 0.01 M; $K_2Cr_2O_7$, 0.00017 M; H_2SO_4, 1.55 M.

% Dichromate reduced	$-\Delta(K_2Cr_2O_7)/\Delta t$ (moles/kg./min.) $\times 10^8$	$k \times 10^3$ calculated from equation (1)
1 to 5	4.5	2.7
5 to 48	5.5	4.4
48 to 53	4.0	4.7
53 to 84	3.5	6.5
84 to 89	1.8	8.2

In all cases, the observed rate in the latter stages of the reaction was several times greater than the rate calculated by equation (1) for the initial reaction. The reaction, therefore, was autocatalyzed as are a large number of oxidations involving organic molecules and oxygen, probably due to the formation of peroxides[5] and easily oxidized products such as the ketone.[1d]

In the photochemical reaction, autocatalysis also occurred.[1b,c] The equation for the initial reaction, however, may be written as

$$(1)^* \quad -\Delta(K_2Cr_2O_7)/\Delta t = k^*(K_2Cr_2O_7)^{1/2} (\text{alkaloid})^0$$
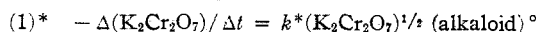
k^* not only varied with the temperature, but also with structural differences in the alkaloids and the wave length and intensity of monochromatic light absorbed by the alkaloids. Light absorbed by the other reactants did not affect the reaction measured. The independence of the photochemical rate upon the concentration of the alkaloid (indicated in $(1)^*$ by (alkaloid)^0) therefore suggested[1c] that one molecule of alkaloid entered the photochemical reaction. $\text{Log}_{10} k^*$ was a linear function of $1/T$ but the slopes of the plots were nearly horizontal, e. g., for quinine at λ 366 mμ, $\log_{10} k^* = a -370/T$, when other variables were fixed.

A comparison of equations $(1)^*$ and (1) shows that the light effective in the photochemical reaction initiates a different reaction (as measured by the disappearance of dichromate) than takes place upon the absorption of thermal energy alone.

Summary

The thermal rates of oxidations of quinine, hydroquinine and cinchonine by dichromic acid in

(5) H. L. J. Bäckstrom, *Medd. Vetenskapsakad. Nobelinst.*, **6**, No. 16, 57 (1927), and his other publications.

←Log$_{10}$ ($-\Delta[K_2Cr_2O_7]/\Delta t$).
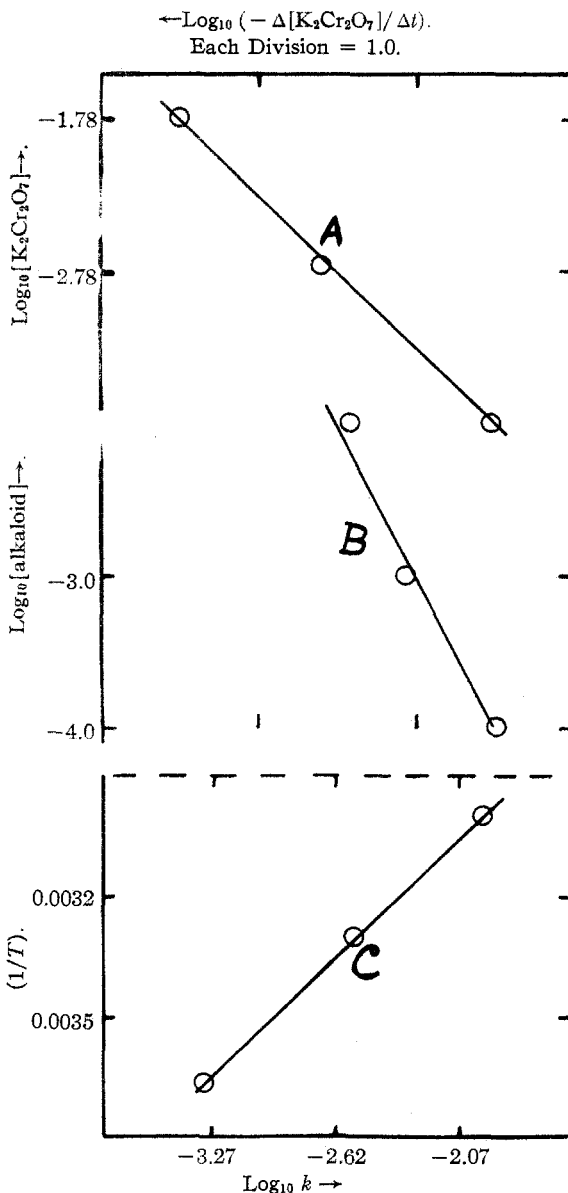Each Division = 1.0.

Fig. 2.—The slopes of the lines in plots A and B, when the logarithm of the rate is taken as the dependent variable, give the order of the initial reaction with respect to the reactant whose concentration is varied. In plot A, the concentration of alkaloid was fixed at 0.01 M and in plot B, dichromate was fixed at 0.00017 M. The activation energy of the reaction equals -4.58 multiplied by the slope of the line in plot C when log$_{10}$ k is taken as the dependent variable.

1.55 M sulfuric acid are the same within 5%. The reactions are autocatalytic.

The initial rates are given by the equations

$$-\Delta(K_2Cr_2O_7)/\Delta t = k(K_2Cr_2O_7) (\text{alkaloid})^{1/2} \quad (1)$$

and

$$\log_{10} k = 4.05 - 2000/T \quad (2)$$

when k is expressed in (kilograms of solution)$^{1/2}$ (moles)$^{-1/2}$ (minutes)$^{-1}$.

Light absorbed by the alkaloids initiates a different reaction which is affected very little by thermal energy.

CAMBRIDGE, MASS.   RECEIVED OCTOBER 6, 1939

The Unesterified Primary Hydroxyls in Acetone Soluble Cellulose Acetate[1]

BY F. B. CRAMER AND C. B. PURVES

It is well known that cellulose triacetate, subjected to a mild hydrolysis, loses some of its original solubilities in organic solvents and acquires new ones, among which a capacity to dissolve in acetone is of great technical importance.[2] Although there have been various opinions as to the cause of this change,[3] it now seems certain that an alteration in the average chain length of the cellulose macromolecule is not necessarily involved.[4] On the other hand, only those acetates which average 2.1 to 2.6 acetyl groups per anhydroglucose unit are soluble in acetone and they must be prepared by the partial hydrolysis of the triacetate rather than by the partial esterification of cellulose.[3,5] These observations suggest that true acetone solubility depends not only upon the numerical ratio of acetyl to hydroxyl groups[6] but also on their relative distribution. Whatever this may be, unesterified hydroxyl is confined to the second, third and sixth positions of the glucose residues and is accordingly of a secondary or a primary alcoholic nature. We have found only one attempt to discriminate chemically between the two possible types of hydroxyl, and this was by determining the molar amount of triphenylmethyl chloride which would condense with commercial acetone-soluble acetate dissolved in pyridine.[7] By assuming that only unesterified primary as opposed to secondary hydroxyls would re-

act under these conditions, approximately one-third of the free hydroxyls were assigned to the primary or sixth position of the glucose units. This assumption was subsequently shown to be unfounded in the case of simple glycosides[8] and the result required confirmation by an independent method.

In the present work, two commercial acetone-soluble cellulose acetates averaging 0.56 and 0.67 mole of free hyroxyl per glucose unit were condensed, in dilute pyridine solution at 20°, with a large excess of p-toluenesulfonyl chloride (tosyl chloride). Samples were isolated at intervals and their sulfur content plotted against time (Fig. 1). About one-third of the hydroxyls were rapidly esterified in the first three hours, then the rate decreased markedly and the tosylation reached a maximum between the third and tenth days, when the reaction was about three-quarters complete. An extremely slow replacement of tosyl groups by chlorine progressed during the subsequent months. The tosylation removed no acetyl groups because the products analyzed for acetyl retained the original quota. It was also improbable that acetyl had wandered from one hydroxyl to another during the reaction, the reagents used not having caused this even with partly acetylated glucoses where such wandering was known to occur readily.[9] The tosyl groups were therefore considered to be faithful reproductions of the positions of the hydroxyls in the original cellulose acetate. In order to determine these positions, it was hoped that the tosylated acetate could be degraded to partly tosylated glucoses, the examination of which would give the desired information. Attempts to accomplish this degradation with hydrogen bromide in glacial acetic acid,[10] with cold

(1) Delivered at the Boston meeting of the American Chemical Society, September, 1939.

(2) Berl and Koerber, THIS JOURNAL, 61, 154 (1939), studied the effect of low temperatures on such solubility relationships.

(3) The earlier work has been reviewed adequately by Krüger in "Zelluloseazetate," Theodor Steinkopff, Dresden-Blasewitz, 1933, pp. 173–178. See also Marsh and Wood, "An Introduction to the Chemistry of Cellulose," Chapman and Hall. Ltd., London, 1938, pp. 200–210.

(4) Staudinger and Daumiller, Ann., 529, 219 (1937). This paper has many literature references.

(5) Direct partial acetylation may give products of limited or temporary solubility or which are too degraded to be of technical value. They are omitted from consideration throughout the present article.

(6) Highfield, Trans. Faraday Soc., 22, 57 (1926).

(7) Sakurada and Kitabatake, J. Soc. Chem. Ind. Japan, 37, (supplementary binding) 604 (1934).

(8) Hockett and Hudson, THIS JOURNAL, 56, 945 (1934).

(9) Helferich, Bredereck and Schneidmüller, Ann., 458, 111 (1927).

(10) Hess, Littmann and Pfleger, ibid., 507, 55 (1933), obtained 2,3,6-tritosylacetobromoglucose in 70% yield from tritosyl starch by using this reagent.