

**Choline Iodide.**—The foregoing ester was reduced with a solution of 2.0 g. (5.2 mmoles) of lithium aluminum hydride in 25 ml. of anhydrous diethyl carbitol. The reaction mixture was decomposed with 30 ml. of butyl carbitol and then heated at 160–180° for four hours. The bath temperature was then raised and about 25 ml. of distillate was collected in an ice-cooled receiver. The distillate was redistilled and the fraction boiling up to 180° was collected. In inactive runs it was found difficult to separate small quantities of diethyl carbitol from the dimethylaminoethanol but the presence of the carbitol did not affect the preparation of the methiodide.

The crude dimethylaminoethanol was allowed to reflux for two to three hours on a steam-bath with methyl iodide. The solid was filtered, washed with dry ethanol and dried; yield 0.420 g. (15.8% based upon starting acetic acid derivatives).

*Anal.* Calcd. for  $C_6H_{14}OI$ : C, 25.98; H, 6.10; I, 54.92. Found: C, 26.25; H, 5.93; I, 55.21.

**Choline Chloride.**—A mixture of 0.752 g. (3.3 mmoles) of choline iodide and 1.0 g. (4.3 mmoles) of silver oxide in 5 ml. of water was shaken for a short while and then allowed to stand overnight. The precipitate was centrifuged and the aqueous layer titrated with 1 *N* hydrochloric acid to a pH of 7. The resulting solution of choline chloride was lyophilized and the residual white solid weighed 396 mg. (87%).

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## The Reaction between Uranium and Oxygen

BY DANIEL CUBICCIOTTI<sup>1</sup>

Uranium tarnishes rapidly at room temperature and its heat of oxidation is large (256 kcal. per mole of  $UO_2$ ). In these respects it is similar to thorium, which has been shown<sup>2</sup> to oxidize by the parabolic law<sup>3</sup> at low temperatures and the linear law at higher temperatures. The present study was made to discover whether the uranium oxidation was similar to that of thorium in changing from parabolic to linear.

### Experimental

The rate of consumption of oxygen by the metal was measured by following the decrease in pressure of oxygen over a sample of metal in a closed container.<sup>2</sup> The one sample used throughout this work was a  $\frac{3}{8}$ " rod of 99.5% pure uranium obtained from the A. D. Mackay Co. under license from the Atomic Energy Commission. The surface of the sample was machined by the shops of the Argonne National Laboratory. Immediately before each oxidation the surface oxide was removed from the sample by abrasion with 400 emery cloth. All oxidations were made at 20 cm. oxygen pressure.

The apparatus used previously<sup>2</sup> was modified because of the large sample size. The sample bulb was a test-tube,  $\frac{5}{8}$ " by 6". It was connected to the measuring manometer with a standard taper ground joint for easy introduction of the sample. The ground joints were outside the furnace. The other end of the manometer was connected to a similar test-tube containing a rod of silicon carbide,  $\frac{3}{8}$ " by 3", used to balance the volume of the uranium rod. The gas volume in the temperature gradient between the furnace and the room was filled as completely as possible with glass rods to minimize fluctuations from changes in the temperature gradient.

(1) North American Aviation, Inc., Downey, California.

(2) P. Levesque and D. Cubicciotti, *THIS JOURNAL*, **73**, 2028 (1951).

(3) For a discussion of the types of oxidation laws see E. A. Gulbransen, *Trans. Electrochem. Soc.*, **91**, 573 (1947). Of interest in the present work are the parabolic law,  $w^2 = kt$ , and the linear law,  $w = k_1t$  in which  $w$  is the weight of oxygen consumed per unit area in time  $t$ ;  $k$  and  $k_1$  are constants. A few of the oxidations of the present work were found to follow an equation  $w^n = k_2t$ , in which  $n < 1$ . This equation is mentioned in the text as a less than first degree equation in the amount of oxygen consumed.

Preliminary experiments showed that a relatively long time was required to heat the sample to temperature. The lower the temperature of a run, the longer heating period necessary. For the lowest temperatures the sample was heated in vacuum for 100 minutes before oxygen was introduced. At the highest temperatures, 30 minute heating periods were used, while at about 160° the period was 60 minutes.

The effect of an insufficient heating period was to introduce a dip in the beginning of the oxidation curve. Campbell and Thomas<sup>4</sup> observed a similar dip with copper from 100 to 300° and showed the cause to be related to outgassing of the sample. To test this idea, one oxidation was stopped by evacuating the oxygen, cooling the sample under vacuum, reheating it for a short period, and then resuming the oxidation by re-admitting oxygen. A dip appeared in that curve. Another oxidation was stopped by evacuating the oxygen and immediately restarting the oxidation without cooling the sample. No dip appeared in that curve. It seemed that the temperature of the sample had more influence on the dip than outgassing.

A possible explanation for the dip in the present work is as follows. If the oxygen is admitted too soon, the temperature of the sample is below that of the furnace and of the reference bulb because the metal absorbs the radiant energy less readily than non-metals. The gas in the reference bulb then expands to its final state before the gas in the sample bulb, causing the initial rise in the oxidation curve. The gas in the sample bulb subsequently expands and lowers the oxidation curve. When the sample finally gets to temperature, it begins to oxidize and gives the curve a parabolic shape.

## Results and Discussion

As with thorium,<sup>2</sup> uranium was found to oxidize according to the parabolic law at low temperatures and according to the linear law at higher temperatures. At still higher temperatures the oxidation curve was lower than first degree in the weight of oxygen consumed. The temperature of the parabolic to linear transition for uranium was lower than that found for thorium.

From 90 to 165° the oxidation was parabolic. The data for several oxidations are given in Fig. 1, plotted as amount of oxygen consumed *versus* the square root of time. Since the curves were straight lines, the oxidations obeyed the parabolic law. From 165 to 215° the oxidations were essen-

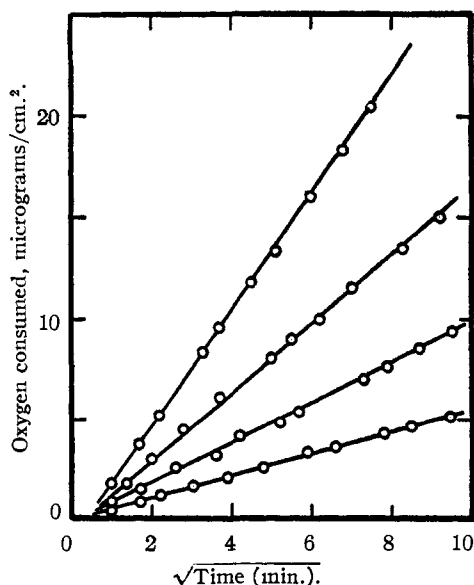


Fig. 1.—The oxidation of uranium at 112, 133, 150 and 167°, parabolic plot.

(4) W. E. Campbell and U. B. Thomas, *ibid.*, **91**, 345 (1947).

tially linear, but above 215° the curves were less than first degree in the amount of oxygen consumed. Figure 2 compares the curves of the parabolic, the linear, and lower degree oxidations. The oxidations from 165 to 220° were all fitted to linear equations even though that range was one of transition from parabolic to linear. From the variation of the logarithm of  $k$  and  $k'$  with reciprocal of absolute temperature activation energies for the parabolic and linear oxidations were found to be 24 and 22 kcal. per mole, respectively. The activation energy of the linear oxidation may have little or no significance since the type of oxidation curve was changing in that region. The oxides formed were dark blue or black for the more extensive oxidations and gold or brown for the slight oxidations.

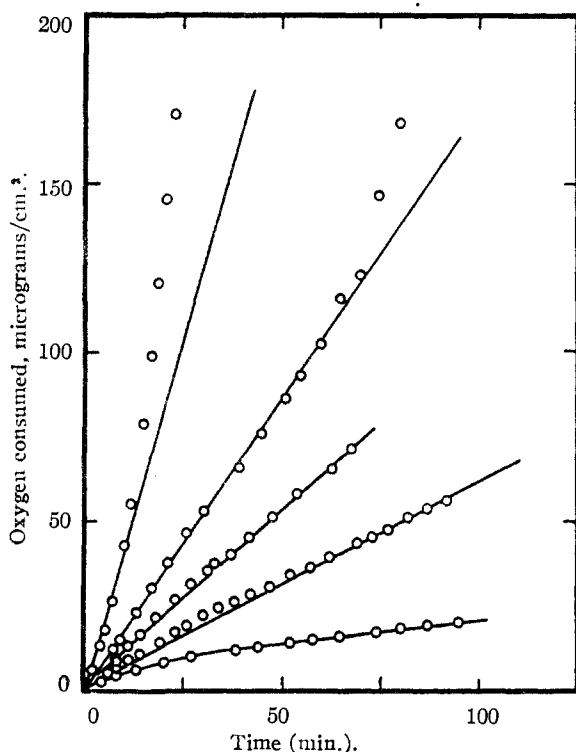


Fig. 2.—The oxidation of uranium at 155, 192, 203, 215 and 237°, linear plot.

The transition of oxidation type from parabolic to linear has been observed with thorium<sup>2</sup> and aluminum<sup>5</sup> as well as the present case of uranium. It was shown that with thorium the temperature of the sample increased above that of the furnace for oxidations above the linear range. It is possible that the linear oxidation was caused by a continuous increase of the sample temperature as the oxidation proceeded. If the sample oxidized parabolically, but at increasing temperature, the resulting oxidation might appear linear.

The increase in sample temperature must be due to a greater rate of influx of heat than outflow. The source of heat is the oxidation itself, while the outflow is mainly by radiation. A comparison of these quantities was made for several metals that oxidize parabolically up to 1000°, such as copper, iron and

(5) E. A. Gulbransen and W. S. Wyson, *J. Phys. Colloid Chem.*, **51**, 1087 (1947).

manganese, and for the metals thorium, aluminum and uranium. The data showed that the metals that undergo transition were less likely to increase in temperature than those that oxidize parabolically. Therefore it seems unlikely that a temperature rise is the cause of the parabolic-linear transition.

An alternative explanation for the transition may be given. Since the volume of oxide formed is larger than that of metal consumed, the oxide is under strain. If the strain is too large, the oxide may crack or flake when the oxide reaches a certain thickness, resulting in an oxidation that is linear or even of lower degree than linear, after the cracking occurs. With increasing temperature the thickness at which the oxide cracks occurs sooner; at a certain temperature the cracking can occur so soon that the entire oxidation appear linear.

To substantiate this hypothesis an oxidation at 237° was interrupted after 25 minutes by evacuating the system. After a 35-minute interval *in vacuo* the reaction was restarted and it continued at a somewhat greater rate than before. A second interruption of 90 minutes had similar results. The data are shown in Fig. 3. If the oxidation had been proceeding at temperatures above that of the furnace, the interruptions would have allowed the specimen to return to the furnace temperature and the oxidation to proceed at a lower rate. If the oxide film had been cracking, then the oxidation would proceed at the same or greater rate, as was the case.

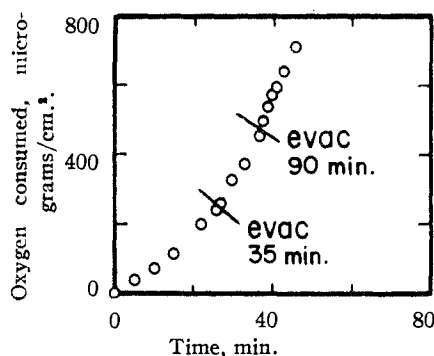


Fig. 3.—Uranium oxidation at 237°, interrupted.

If the film-cracking hypothesis is correct, then a long oxidation that started parabolically would

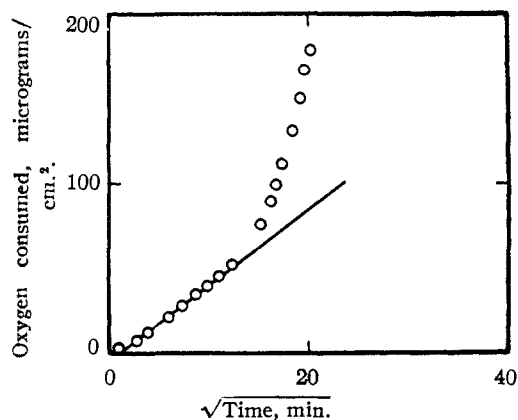


Fig. 4.—Long oxidation at 170°.

eventually become linear. A long oxidation at 170° is shown in Fig. 4. The initially parabolic oxidation became more rapid than parabolic after 100 minutes.

Thus there is some evidence in favor of the film-cracking hypothesis. Further investigation should be made to test it.

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### On Halsey's New Multilayer Adsorption Equation

By W. KEITH HALL

In a recent paper,<sup>1</sup> Halsey derived a multilayer isotherm involving the following assumptions: (1) The source of the van der Waals energy,  $\Delta E$ , has its origin one adsorbate diameter below the center of the first adsorbed layer. (2)  $\Delta E$  decays with the third power of the distance from the surface. (3) Regions of equal  $\Delta E$  are localized into large enough patches so that edge effects may be neglected.

The first two of these assumptions are incompatible. The  $r^{-3}$  law for van der Waals attractive energy near a surface arises from the  $r^{-6}$  law for two isolated atoms or molecules by integrating over the entire volume of the solid, treating it as a continuous medium.<sup>2</sup> In surface chemistry it is usually assumed that the surface "sites" have considerably greater attractive energy than the underlying layers and, if this is the case, the attractive energy could be closely approximated by integration over the surface layer only. This, however, leads to an  $r^{-4}$  law. Halsey's use of the  $r^{-3}$  law implies that each layer of atoms in the solid has the same attractive power as the surface layer, *i.e.*, the patches of constant energy are piers extending into the solid to a considerable depth. This is in contradiction to assumption (1).

Use of the  $r^{-4}$  law would make very little difference in the derivation of Halsey's equation (13), which will become

$$\theta = \exp \{ +\Delta E_0/\Delta E_m \} \sum_{n=1}^{\infty} Z^n \quad (13')$$

The series will converge more rapidly, and so the shape of the calculated isotherms, for a given set of parameters, will be somewhat changed in the direction of greater steepness as the liquefaction pressure is approached. The flat portions will become visible at the same relative pressures, but will extend over a greater pressure range and appear at higher values of  $\exp \{ -\Delta E_0/\Delta E_m \}$ .

Alternatively, use of the  $r^{-3}$  law requires that one have an exponential distribution of three dimensional patches of different adsorption energies, severely restricting the concept of a "site."

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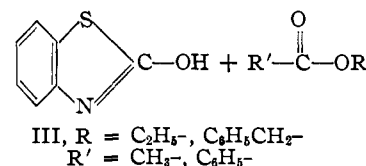
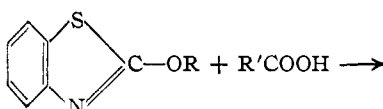
(1) Halsey, *This Journal*, **73**, 2693 (1951).

(2) Brunauer, "The Adsorption of Gases and Vapors," Vol. I, Princeton University Press, Princeton, N. J., 1945, p. 205.

### The Effect of Some Organic Acids on Alkyl Heterocyclic Ethers

By HENRY GILMAN, KENNETH E. LENTZ AND JOHN A. BEEL

The cleavage of 2-alkoxyquinoline and 2-alkoxybenzothiazole compounds by aryl thiols at 170° to form 2-hydroxy derivatives of the heterocycles and alkyl aryl sulfides has recently been reported.<sup>1</sup> We have now carried out further investigations of this reaction in order to determine the effect of varying strengths of acids. In this study the only acids which effected a cleavage similar to that of the thiols<sup>1</sup> were carboxylic acids. Thus, acetic and benzoic acids reacted with 2-ethoxybenzothiazole (I) and 2-benzyloxybenzothiazole (II) to form 32 to 85% yields of 2-hydroxybenzothiazole (III) and the corresponding esters. Oxalic acid has



been shown to react similarly with alkyl aryl ethers.<sup>2</sup>

Phenolic analogs of the thiols, phenol, *p*-cresol and  $\beta$ -naphthol, did not cleave I or II, and in most instances the recovery of starting material was high. However, no II was recovered in the reaction with  $\beta$ -naphthol even though no cleavage products were isolated. Following the discovery that these phenols were unreactive, experiments were conducted employing the more strongly acidic *p*-nitrophenol. Again the expected alkyl aryl ethers were not obtained though the recovery of starting material was significantly low. *p*-Nitrophenol has been found to react with piperidino-methyl ethyl ether to give an ortho-substituted phenol.<sup>3</sup>

From our results the *pKa* values of the reagents were not significant. Barbituric acid with a *pKa* value less than that of benzoic or acetic acid (see Table I) was almost completely recovered from the reaction with I. The weakly acidic sulfhydryl compounds exhibited an especial reactivity which has been shown previously in reactions with triethylbismuth and tetraethyllead.<sup>4</sup> Two other compounds, 1,3-diphenyl-1,3-propanedione ( $\beta$ -hydroxychalcone) and fluorene were found to be unreactive.

#### Experimental

**Cleavage Reactions.**—The heterocyclic ether was mixed in a molar ratio 1:1 to 1:3 with the acidic reagent and heated with vigorous stirring in a dry nitrogen atmosphere for 15 to 48 hours. The 2-hydroxy derivative separated from the reaction mixture on cooling, if cleavage had occurred. Frequently the acidic reagent would separate when there had been little or no reaction. Any solid material was isolated

(1) G. Illuminati and H. Gilman, *This Journal*, **71**, 3349 (1949).

(2) E. Waser and K. Sander, *Helv. Chim. Acta*, **8**, 106 (1925).

(3) C. Yang, *J. Org. Chem.*, **10**, 67 (1945).

(4) H. Gilman and J. F. Nelson, *This Journal*, **59**, 935 (1937).