of the adenine nucleosides. In view of the several assumptions and the stratagem of using one allowed range of the torsion angle (10 to −60°) and ignoring the other allowed range (−80 to −140°),[27] the results to date cannot be cited as conclusive evidence that the preferred conformation for the sugar ring is *anti*. The results are offered as an indication in favor of this conformation and have additional value in that they provide insight into the factors which contribute to the rotational strength and they suggest future experiments that may give more definitive information.

Acknowledgment. The authors wish to acknowledge the National Institutes of Health Research Grant GM-12862-02 and the National Cancer Institute of the National Institutes of Health Research Grant CA-08109-02 for financial support relative to the present study. We also wish to thank Dr. Dan Urry and the Institute for Biomedical Research for the use of the Cary 6001 circular dichroism attachment to the Cary 60 and for the use of their computer facilities. This paper was taken in part from the Ph.D. Thesis of D. W. Miles, University of Utah, 1967.

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(27) However, from σ-bond moments and π-bond moments and bond lengths, a charge of -0.87×10^{-19} and -0.7×10^{-19} C is found to be on the N-3 of the adenine ring and the furanose ring oxygen, respectively. This interaction is expected to stabilize the adenosine derivatives in the 10 to −60° range.

Kinetics and Mechanism of the Reaction between Bromine Trifluoride Vapor and Uranium Tetrafluoride

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The reaction between BrF_3 vapor and UF_4 was investigated in the temperature range from room temperature to 300° and a range of BrF_3 partial pressure from 6 to 45 mm. Argon saturated with BrF_3 vapor was introduced into a reactor at a fixed flow rate, and the BrF_3 was treated with the UF_4, the weight change of which was measured by a thermobalance. The reaction mechanism was also studied and UF_5 and UF_{4+x} $(0 < x < 1)$ were captured as the intermediates of the reaction. From these experiments it was found that (1) the reaction proceeded even at room temperature; (2) the rate of reaction was proportional to the BrF_3 partial pressure and changed little with increasing temperature; (3) at temperatures below 100°, UF_4 was converted to UF_6 through the reaction $UF_4 \rightarrow UF_{4+x}$ $(0 < x < 1)$ $\rightarrow UF_5 \rightarrow UF_6$, at temperatures of 100–200°; however, the reaction mechanism was complicated, probably due to the occurrence of an interaction between the produced UF_6 and the remaining UF_4; and (4) owing to this temperature dependence of the reaction mechanism, the rate constant, calculated from the slope of the weight loss *vs.* time curve, rose to a peak at 185° and then fell to a minimum at 220°. The activation energy, calculated from the Arrhenius equation, has a low value of 1.0 kcal/mol.

Introduction

Interhalogen compounds such as chlorine trifluoride, bromine trifluoride, and bromine pentafluoride convert many uranium compounds to uranium hexafluoride.[1-4] As compared with the reactions between uranium compounds and elemental fluorine,[5,6] these reactions proceed even at considerably lower temperatures, and the resulting activation energies, calculated from each Arrhenius plot, generally show smaller values.

In addition, in some of these reactions, an unusual behavior of the reaction rate has been reported: for the reaction between UF_4 and ClF_3, Labaton has reported that the reaction rate passed through a maximum at 105°, fell to a minimum at 148°, and then rose again.[1] For this he has explained that the reduced rate between 105 and 148° was due to a lower rate of the reaction of ClF_3 with a UF_{4+x} surface, produced as an intermediate, rather than with a UF_4 surface.[1] A

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(1) V. Y. Labaton, *J. Inorg. Nucl. Chem.*, **10**, 86 (1959).

(2) N. S. Nikolaev and Yu. D. Shishkov, *Proc. Acad. Sci. USSR, Chem. Sec.* (English Transl.), **143**, 168 (1962).

(3) M. Iwasaki and T. Sakurai, *J. Nucl. Sci. Technol.*, **2**, 225 (1965).

(4) R. L. Jarry and M. J. Steindler, *J. Inorg. Nucl. Chem.*, **29**, 1591 (1967).

(5) V. Y. Labaton and K. D. B. Johnson, *ibid.*, **10**, 74 (1959).

(6) M. Iwasaki, *ibid.*, **26**, 1853 (1964).

similar phenomenon has been reported by Nikolaev and Shishkov for the UF_4–ClF_3 reaction.[2] On the other hand, for the reaction between U_3O_8 and BrF_3, previously reported by the authors, the reaction rate rose to a peak at 200° and then fell to a minimum at 225°, for which no cause has yet been clarified.[3]

The present work was carried out to ascertain whether such an anomaly of the rate constant as in the UF_4–ClF_3 reaction also appears in the reaction between UF_4 and gaseous BrF_3 and to obtain further information about these anomalies. Experiments were mostly concerned with the kinetic study of the reaction by use of a thermobalance, and its mechanism was also studied.

Experimental Materials and Procedure

1. *Materials. Bromine Trifluoride.* Commercial grade bromine trifluoride, from the Harshaw Chemical Co., was purified by distillation, as reported previously.[7]

Uranium Tetrafluoride. Fine powder of UF_4, was provided by Mitsubishi Kinzoku Kogyo Co., Ltd., of 98% purity, the remaining 2% being uranium dioxide and uranylfluoride. The purity is almost the same as that of uranium tetrafluoride generally used for kinetic studies of fluorination by other investigators.[1,4,5] The small amount of these impurities does not affect the validity of the experiments, as possible weight changes of these impurities would be very small and within the experimental accuracy.

Sedimentograph analysis showed that the particle sizes were distributed in the range below 10 μ. The surface area, determined by krypton adsorption, was 1.0 m^2/g. The water content, determined by infrared spectrophotometry, was negligibly small, *viz.* 0.25%. The sample was used without further purification.

2. Procedure. The apparatus and procedure were similar to those used previously.[3] However, improvements were made on the apparatus in order to prevent corrosion by bromine trifluoride. In the thermobalance previously used, the spring column was made of a glass tube and the argon stream was brought into the reaction tube from the top of the spring column to protect the spring column from attack by BrF_3 from the convection currents set up in the reaction tube. However, at reaction temperatures above 200°, the spring column was considerably corroded by the BrF_3 in the hot convection currents.

In the thermobalance used in the present work, the spring column was made of a Kel-F or Teflon tube, and the sensing element was a nickel-plated phosphor-bronze spring, the extension of which was measured by a differential transformer and recorded automatically.[8] Therefore, all of the surfaces in contact with the reactant gas in the thermobalance were made of materials not affected by BrF_3. The detailed diagram of the thermobalance is shown in Figure 1. The spring column was maintained at a temperature a little above the temperature of the thermostat (to be described below) by means of a thermostated air bath in order to keep the column temperature from affecting the spring sensitivity and to prevent condensation of the BrF_3 vapor. The accuracy of the thermobalance was 1 mg for weight changes up to 100 mg.

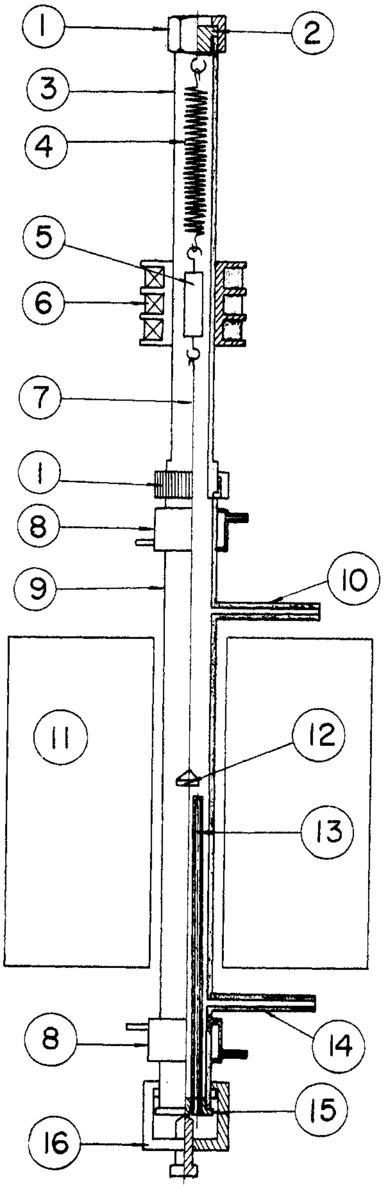

Figure 1. Diagram of the thermobalance: 1, nut; 2, Kel-F block provided with a hook; 3, Kel-F tube; 4, nickel-plated phosphor-bronze spring; 5, ferrite core of differential transformer (sealed by Teflon-100X tube); 6, differential transformer; 7, nickel wire; 8, cooling water jacket; 9, monel reactor tube; 10, reactant-gas inlet; 11, electric furnace; 12, sample pan; 13, monel thermocouple well; 14, gas outlet; 15, cover of reactor tube; 16, device to close the cover.

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(7) T. Sakurai, Y. Kobayashi, and M. Iwasaki, *J. Nucl. Sci. Technol.*, **3**, 10 (1966).

(8) S. Tsujimura, G. Fujisawa, and A. Takahashi, Japan Atomic Energy Research Institute Report No. 1070, Tokyo, 1964.

From the desired spring movement, the amount of uranium tetrafluoride used in a run was fixed between 76 and 78 mg; the bed was about 0.7 mm deep. However, in order to see the effect of the amount of the sample on the reaction rate, various weights of sample between 30 and 180 mg were used in various runs by replacing this spring with another.

Bromine trifluoride vapor was supplied to the reaction tube in the following manner, using argon as the carrier gas. Liquid bromine trifluoride, 70–80 mm deep in a bubbling vessel, was bubbled by the argon stream with a fixed flow rate and was vaporized into that stream. The argon, containing the BrF_3 vapor, was then introduced into a thermostat; during the passage through the thermostat, the argon was saturated with the BrF_3 vapor because the thermostat was of a lower temperature than the liquid BrF_3 in the bubbling vessel. The argon saturated with BrF_3 vapor was introduced into the reaction tube at a constant flow rate, and the uranium tetrafluoride sample was fluorinated to UF_6 by the BrF_3. All the paths taken by the BrF_3 vapor were heated to prevent condensation of the BrF_3 vapor.

Prior to the kinetic studies, the partial pressure of BrF_3 in the carrier gas from the thermostat was checked, using He as the carrier gas. Keeping the temperature of the thermostat at 50 ± 0.5° and that of the liquid BrF_3 at 65 ± 1°, He gas was passed through the system at constant flow rates between 10 and 15 l./hr, and the BrF_3, contained in the gas exitting from the thermostat, was collected in a liquid nitrogen cold trap every 10 min. Consequently, 0.42–0.64 g of bromine trifluoride was collected in the cold trap, depending upon the flow rates of He gas. From the amounts of the collected bromine trifluoride, the vapor pressure of BrF_3 in the He gas was calculated to be 34 ± 2 mm; the ±2 mm corresponds to a deviation of ±5.9%. The value is very close to that of the corresponding saturation vapor pressure of BrF_3 (33 mm) calculated from the empirical formula obtained by Oliver and Grisard.[9]

Hence, it is considered that the vapor pressure of BrF_3 in the carrier gas is kept constant, with deviations of less than ±6%, in the range of the flow rates described above. This small deviation does not affect the validity of the experiments, as will be discussed later, and the following kinetic studies were carried out with the assumption that the carrier gas was saturated with BrF_3 vapor.

Results and Discussion

1. Kinetics of the Reaction. In most of the literature on the kinetics of fluorination reactions of uranium compounds, in which the products are entirely gaseous, the results are treated using the diminishing sphere model.[10] In this kinetic model, the reaction rate is expressed by

$$-\frac{\mathrm{d}M}{\mathrm{d}t} = k(4\pi r^2) \qquad (1)$$

where M and r are the mass and radius of the reacting particle at time t, and k is the rate constant for a given temperature and partial pressure of the reactant gas. The final equation derived is

$$(1 - F)^{1/3} = 1 - k't \qquad (2)$$

where F is the fraction of reacted solid; k' is a reaction rate constant, related to the rate constant in eq 1 by the expression $k' = k/r_0\mu$ (r_0 = initial radius and μ = the bulk density of the particle). Therefore, the rate constant k' is obtained from the slope of straight line in a graph of the value $(1 - F)^{1/3}$ *vs.* time.

However, in the present experiments, a plot of $(1 - F)^{1/3}$ *vs.* time did not give a straight line in the part of curve, which excludes the beginning of the reaction where the plot of $(1 - F)^{1/3}$ *vs.* time deviated from the straight line for the time required for the reactant gas to replace the inert gas in the reaction tube.[1,5,10] This seemed to be due to the bed depth of the sample uranium tetrafluoride in the pan, since a bed depth of 0.7 mm was considerably thick compared with the particle sizes of the uranium tetrafluoride. In such a case, it has been indicated by other authors that a plot of $(1 - F)$ *vs.* time gives a straight line, except the portion at the end of the reaction where $(1 - F)^{1/3}$ gives a better fit.[10]

In Figure 2, the values of $(1 - F)$ and $(1 - F)^{1/3}$ for a typical run are plotted against time. Also, in the present experiments, a plot of $(1 - F)$ *vs.* time gave a straight line, except the portions at the beginning and end of the reaction. This means that the rate of reaction is expressed as

$$-\frac{\mathrm{d}W}{\mathrm{d}t} = K \qquad (3)$$

where W is the weight of the solid reactant at time t, and K is a constant. The reason is that eq 3 takes the following form, when integrated

$$(1 - F) = 1 - (K/W_0)t \qquad (4)$$

where W_0 is the initial weight of the solid reactant.

On the other hand, when the reaction was stopped before completion, it was found that the remaining material in the pan, the color of which was dark brown, had caked considerably.

From these facts, it is considered that, owing to the thickness of the bed of the solid reactant and its caking during the process of the reaction, the diminishing-sphere model is not applicable in the present experiments and a plot of $(1 - F)$ *vs.* time shows a better fit. In other words, in the present experiments, it seems that UF_6 is produced in a relatively thin layer at the surface

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[9] G. D. Oliver and J. W. Grisard, *J. Amer. Chem. Soc.*, **74**, 2705 (1952).

[10] C. E. Johnson and J. Fischer, *J. Phys. Chem.*, **65**, 1849 (1961).

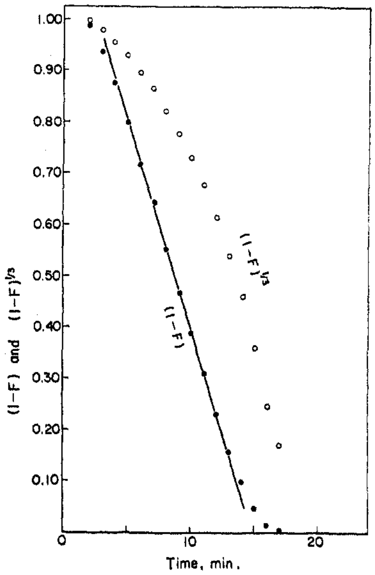

Figure 2. Plots of $(1 - F)$ and $(1 - F)^{1/3}$ *vs.* time: initial weight of UF_4 = 77 mg, partial pressure of BrF_3 = 15 mm, gas velocity = 55.4 cm/min, temp = 110°.

of the bed and, for this, the thickness of the bed decreases with time at the rate determined by the reaction temperature and the BrF_3 partial pressure.

In a plot of $(1 - F)$ *vs.* time, the deviation at the beginning of a run is explained by the experimental conditions used. The reaction tube is initially filled with argon, and it takes 3-4 min for the argon–BrF_3 mixture in the reaction tube to become the value fixed for the run. Consequently, the reaction rate at the beginning of the reaction is considerably low.

The causes of deviation at the end of the reaction were not clarified thoroughly, however, one of the causes may be that, owing to the small amount of the sample remaining, the rate of reaction reverts to a diminishing-sphere model.[10]

Therefore, in the following experiments, the constant K in eq 3 and 4 was used as the rate constant in the treatment of the kinetics of the reaction.

2. Influence of Gas Velocity. The effect of gas velocity on the reaction rate was checked at a given reaction temperature, with the partial pressure of bromine trifluoride kept constant. The velocity of argon in the reaction tube varied from 17.7 to 55.4 cm/min, keeping the BrF_3 partial pressure at 15 mm.

The results are shown in Table I. It is evident that the diffusion rate of bromine trifluoride in the gaseous phase has no effect on the reaction rate, as long as the gas velocity exceeds 45 cm/min. Therefore, in the following experiments, the velocity of argon was fixed at 55 cm/min, that is, an argon flow rate of 15 l./hr.

3. Influence of the Partial Pressure of BrF_3. In several runs, the BrF_3 partial pressure was varied from 7 to 45 mm by changing the temperature of the thermostat and of the liquid BrF_3 in the bubbling vessel, in accordance with the required partial pressures.[9]

Table I: Effect of Gas Velocity on the Rate Constant[a]

Gas velocity, cm/min	Gas flow rate, l./hr	Rate constant (10^3K),[b] g/min
17.7	4.8	4.9
28.0	7.6	5.4
36.9	10.0	5.6 ± 0.1
45.8	12.4	6.2 ± 0.1
55.4	15.0	6.2 ± 0.4

[a] Initial weight of UF_4, 77 ± 1 mg; temperature, 110°; partial pressure of BrF_3, 15 mm. [b] Each value averaged.

Table II shows the effect of the partial pressure of BrF_3 on the reaction rate at a temperature of 110°. This effect can be expressed approximately in the form

$$K \text{ (g/min)} = (6.96 \times 10^{-4})P^{0.8} \text{ (mm)} \qquad (5)$$

4. Influence of Temperature. In the present work, effort was mostly devoted to the clarification of the temperature dependence of the reaction rate.

The 76–78 mg of the uranium tetrafluoride was allowed to react in the temperature range 50-300°, keeping constant the partial pressure of bromine trifluoride (15 mm).

Table II: Effect of Partial Pressure of BrF_3 on the Rate Constant at 110°[a]

Partial pressure of BrF_3, mm	Rate constant[b] (10^3K), g/min	Reaction period[b] min
7	2.2 ± 0.3	44
10	4.6 ± 0.2	24 ± 1
15	6.2 ± 0.5	17
22	8.0 ± 0.3	14
31	11.4 ± 0.4	12 ± 1
45	14.5 ± 0.3	7

[a] Initial weight of UF_4, 77 ± 1 mg; gas velocity, 55.4 cm/min.
[b] Each value averaged.

Typical examples of the weight loss *vs.* time curves at different temperatures are shown in Figure 3. At temperatures below 80°, the rate of reaction was small and the reaction stopped halfway, as shown by the curve of 55°. However, the reaction proceeded rapidly at temperatures above 90°, and the weight loss *vs.* time curves changed in shape with increasing temperature. Thus at temperatures near 185°, the curve, as shown in Figure 3, had a characteristic, in that an induction period appeared in the initial stage of the reaction, *i.e.*, for the initial 7 min, and then the weight loss increased rapidly. At temperatures above 220°, the induction period disappeared again, and the weight loss increased steadily with time, as shown by the curve of 240° in

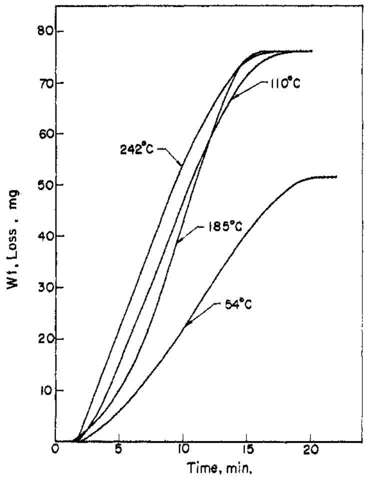

Figure 3. Weight loss *vs.* time curves at different temperatures: initial weight of UF_4 = 77 ± 1 mg, partial pressure of BrF_3 = 15 mm, gas velocity = 55.4 cm/min.

Figure 3. On the other hand, the reaction period was almost constant in the temperature range described already, that is, for each 75 mg of the sample, 17 ± 1 min at 110° and 16 ± 1 min in the range of 185–240°.

In several runs, the amount of uranium tetrafluoride was varied in the range of 30–180 mg, but the shape of the weight loss *vs.* time curve at each temperature did not change remarkably, although the reaction period changed in proportion to the amount of the sample used.

These facts indicate that the mechanism of the reaction changes with temperature, the details of which will be discussed later.

In Figure 4, the rate constant K is plotted against the temperature; the constant K was calculated from the graph of the plot of $(1 - F)$ *vs.* time, using eq 4. The rate constant increased with increasing temperature up to 185°, fell to a minimum at 220°, and then remained almost the same thereafter; the relation is similar to that of the reaction of ClF_3 with UF_4 and of BrF_3 with U_3O_8.[1-3]

This relation between the rate constant and temperature is not influenced significantly by the previously described deviation of the partial pressure of BrF_3 in the carrier gas, since the resulting deviation of rate constant K, calculated from eq 5, is 5%, which is within the observed deviation of the K in Figure 4.

In Figure 5, the Arrhenius plot for the reaction is shown in the range 90–190°, from which the activation energy was calculated to be 1.0 kcal/mol. The value is much lower than that for the UF_4–F_2 reaction, which is 15.5–19.9 kcal/mole,[5] and it is close to that of 3.4–5.6 kcal/mol for the UF_4–ClF_3 reaction.[1]

From the value of the activation energy and eq 5, the following equation was derived to represent the temperature and BrF_3 partial pressure dependence of the present reaction, in the temperature range 90–190° and in the BrF_3 partial pressure range of 7–45 mm.

$$\ln K = 0.8 \ln P - (0.49 \times 10^3)(1/T) - 5.98 \quad (6)$$

5. Intermediates of the Reaction. To observe the processes of the reaction, the uranium tetrafluoride was treated in a horizontal reaction tube made of a translucent Kel-F tube (o.d. 10 mm and i.d. 7 mm).

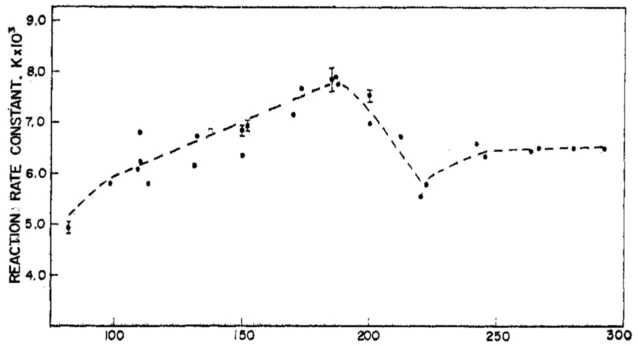

Figure 4. Temperature dependence of the rate constant K: initial weight of UF_4 = 77 ± 1 mg, partial pressure of BrF_3 = 15 mm, gas velocity = 55.4 cm/min.

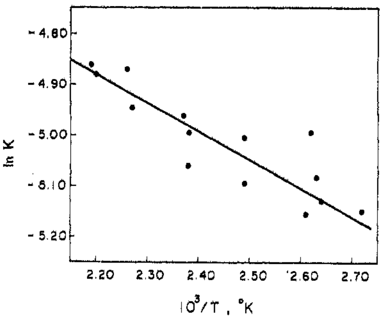

Figure 5. Arrhenius plot for the region 90–190°.

After 100–200 mg of the sample was placed in the reaction tube, argon containing 10 mm of the BrF_3 partial pressure was passed through the reaction tube. Consequently, when the argon–BrF_3 mixture was brought into the reaction tube, the color of the sample changed to dark brown within 3 min and then changed to whitish yellow from dark brown within 30 min, during which the amount of the material decreased very slowly owing to the conversion to UF_6.

Both the dark brown and whitish yellow materials were unstable in air, and their colors turned green upon exposure to air. Identification by X-ray diffraction was done on both the materials, after sealing in thin-walled glass capillaries in a glove box filled with argon. X-Ray diffraction patterns of the whitish yellow material were in agreement with that of β-UF_5, reported by Zachariasen,[11] whereas the patterns of the dark brown one agree with that of UF_4. However, when added to water, the dark brown material was found through chemical analysis to be hydrolyzed and to produce

[11] W. H. Zachariasen, *Acta Crystallogr.*, **2**, 296 (1949).

UO_2F_2 and UF_4. Therefore, the dark-brown material should be also an intermediate of the reaction, *i.e.*, UF_{4+x} $(0 < x < 1)$, since it has been known that intermediate uranium fluorides (U_4F_{17}, U_2F_9, and UF_5) react with water producing UO_2F_2, UF_4, and HF, *e.g.*[12]

$$2U_4F_{17} + 2H_2O \longrightarrow UO_2^{2+} + 7UF_4 + 4HF + 2F^-$$

Hence, at near room temperatures, the reaction seems to proceed through the following three steps

$$6UF_4 + 2xBrF_3 \longrightarrow 6UF_{4+x} + xBr_2 \quad (0 < x < 1) \qquad (A)$$

$$6UF_{4+x} + 2(1 - x)BrF_3 \longrightarrow 6UF_5 + (1 - x)Br_2 \qquad (B)$$

$$6UF_5 + 2BrF_3 \longrightarrow 6UF_6 + Br_2 \qquad (C)$$

In these steps, as seen by direct observation, step A proceeds much more rapidly than the other steps.

6. *Mechanism of the Reaction.* From the results obtained in the above experiments, the following conclusions concerning the mechanism of the reaction can be drawn.

In the temperature range from room temperature to near 100°, the reaction proceeds by the three steps already described, in which step A proceeds much more rapidly than the others.

However, at temperatures above 100°, the mechanism of the reaction becomes considerably complicated. The cause cannot be explained by assuming that the reaction also proceeds by the three steps at temperatures above 100°.

To obtain an insight into the temperature dependence of the mechanism, it is advantageous to utilize a differential curve of the weight loss *vs.* time curve, *i.e.*, the rate of weight loss *vs.* time curve. In Figure 6, typical examples of the differential curves at different temperatures are shown, which were calculated from each weight loss *vs.* time curve. Comparing the curves in Figure 6, the following facts are found.

(i) The differential curves at temperatures above 220° are similar in shape to those at 98 and 110°.

(ii) The differential curve at 185° is remarkable in that an induction period appears in the initial stage of the run and then the rate of weight loss increases abruptly up to a maximum which is the largest in all the curves.

From the results, it seems that, in the reaction near 185°, the UF_6 produced in the initial stage tends to be retained in the remaining sample for some length of time, without immediate evaporation, and then evaporates together with the UF_6 produced in the next stage; that is, an interaction occurs between the produced UF_6 and the remaining material.

As to the reaction between UF_6 and UF_4, the following facts have been reported.[12]

(i) The reaction occurs at temperatures above 100°, producing such intermediate fluorides as UF_5, U_2F_9, and U_4F_{17}.

(ii) At a fixed vapor pressure of UF_6, the resulting product is UF_5 at relatively low temperatures, while at elevated temperatures above 200°, it is U_2F_9 or U_4F_{17}; that is, the amount of UF_6 reacting with a unit mass of UF_4 decreases with increasing temperature at temperatures above near 200°.

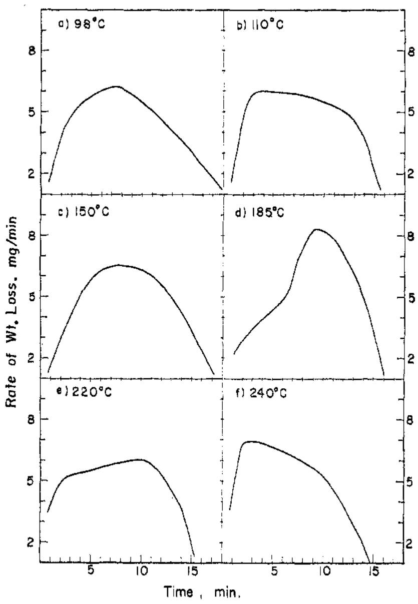

Figure 6. Differential curves of the weight loss *vs.* time curves at different temperatures: initial weight of UF_4 = 77 ± 1 mg, partial pressure of BrF_3 = 15 mm, gas velocity = 55.4 cm/min.

From these facts and from the shapes of the curves in Figure 6, it is concluded that the UF_6 produced in the initial stage of the reaction reacts with the remaining UF_4 at temperatures above 100°, and its reaction rate rises to a peak at 185°.

Hence, in the weight loss *vs.* time curve at 185°, the initial induction period indicates that, during the time, the reaction

$$UF_4 + UF_6 \longrightarrow 2UF_5 \qquad (D)$$

proceeds simultaneously with steps A–C, and the rapid increase of weight loss in the next portion indicates that the over-all reaction proceeds through steps B and C, owing to the disappearance of UF_4.

On the other hand, at temperatures above 200°, since the amount of UF_6 consumed by the remaining UF_4 decreases with increasing temperature, the weight loss *vs.* time curves and their differential curves approach those near 100° in shape.

Thus because of this temperature dependence of the mechanism of reaction, the rate constant K, calculated from each weight loss *vs.* time curve, passes through a maximum at 185° and then falls to a minimum at 220°, as shown in Figure 4. The minimum point at 220° corresponds to the transition point of the mecha-

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(12) J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium, The Element, Its Binary and Related Compounds," Dover Publications, Inc., New York, N. Y., 1961, pp 382–392.

nism of reaction from the UF_6–UF_4 interaction to noninteraction.

Acknowledgment. Thanks are due to Mr. S. Tsujimura, Mr. A. Takahashi, and Mr. G. Fujisawa for their aid in the construction of the thermobalance, and to Dr. S. Suzuki and other members of the Analytical Section, Japan Atomic Fuel Corp., for their analysis of the water content in the sample of uranium tetrafluoride.

Oxidation of Thiourea and Thioacetamide by Alkaline Hexacyanoferrate(III)

by M. C. Agrawal and S. P. Mushran

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Kinetics of the oxidation of thiourea and thioacetamide with alkaline hexacyanoferrate(III) has been studied in aqueous solution. The reaction with thiourea has been found to be first order with respect to thiourea, hexacyanoferrate(III), and hydroxyl ion, while that with thioacetamide shows zero-order dependence on $Fe(CN)_6^{3-}$ and first-order dependence on both thioacetamide and OH^- ion. Potassium chloride concentrations showed accelerating effect on the reaction rate, while the effect of ferrocyanide ion concentration was negligible. Increase in dielectric constant (D) enhanced the reaction rate and the plot of log k against $1/D$ showed a linear relation. A suitable mechanism for the oxidation processes has been proposed.

Introduction

Hexacyanoferrate(III) is well known for its oxidative power in alkaline media and can be described as one of the efficient electron-abstracting reagents. Though uncatalyzed oxidations by hexacyanoferrate(III) ion are, in general, fairly fast, osmium(VIII) ion has been observed to exert a positive catalytic influence, and several inorganic and organic substances may directly be titrated against hexacyanoferrate(III) in its presence.[1]

The kinetics of the oxidation of 3-mercaptopropionic acid has been studied by Bohning and Weiss,[2] while Kolthoff and coworkers[3] have investigated the mechanism of oxidation of 2-mercaptoethanol by hexacyanoferrate(III) in acid medium. In another publication, Kolthoff and coworkers[4] have studied the oxidation of *n*-octyl mercaptan by alkaline hexacyanoferrate(III) in acetone–water medium. Recently, Gorin and Godwin[5] have suggested that the oxidation of some mercaptans is catalyzed by metal ions. In spite of the above work, the literature on the kinetics of oxidation reactions of organic sulfur compounds by hexacyanoferrate(III) appears to be scanty.

In the present communication, the kinetics of the oxidation of thiourea and thioacetamide by alkaline hexacyanoferrate(III) has been investigated in some detail, in order to shed some further light on oxidation mechanisms involving hexacyanoferrate(III) ion. The reactions have been studied in presence of sodium carbonate–bicarbonate buffer, to avoid the effects of any possible pH variations during the progress of the reactions. Influence of several variable factors such as dielectric constant and the concentrations of potassium chloride, potassium hexacyanoferrate(II), and hydroxyl ion has been investigated to ascertain the exact nature of the oxidation processes.

Experimental Section

Materials. (i) Aqueous potassium hexacyanoferrate(III) was prepared from an AnalaR BDH sample and the concentration was checked by iodometry.[6] (ii) Aqueous thiourea was prepared from a *pro analysi* E. Merck reagent. (iii) Aqueous thioacetamide was also prepared from a *pro analysi* E. Merck sample. (iv) All other reagents were of analytical grade. (v) Doubly distilled water was employed for preparing solutions and for diluting where necessary, and in every case glass vessels of Jena Geratglas were

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