Kinetics of Dissolution of β-Uranium Trioxide in Acid and Carbonate Solutions

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The kinetics of dissolution of β-UO_3 in acid and carbonate solutions have been studied as functions of stirring rate, hydrogen-ion concentration, carbonate concentration, various other cations and anions in solution, and temperature. The dissolution rates are: (*i*) independent of stirring rate, (*ii*) dependent on the 0.5 order in [H^+] in acid solutions and a substantially lower order in carbonate solutions; (*iii*) inhibited by the presence of cations in solution in the order Mg^{2+} > Li^+ > Na^+ > [NH_4]$^+$ > K^+ $\geqslant$ Cs^+ in acid solutions and Na^+ > [NH_4]$^+$ > Cs^+ $\geqslant$ K^+ in carbonate solutions, the relative effects of the cations in the acid and carbonate solutions being very similar; (*iv*) increased by sulphate but unaffected by chloride, nitrate, and perchlorate ions in acid solutions; and (*v*) characterised by activation energies of *ca*. 12 kcal mol^{-1} in acid solutions and 15 kcal mol^{-1} in carbonate solutions. The observed kinetic data have been rationalised in terms of a charge-transfer (c.t.) mechanism, in which the transfer of charged complexes of the uranyl and oxide ions of the β-UO_3 lattice across the electrochemical-potential barrier at the solid–solution phase boundary is the rate determining step during the dissolution reaction. In HCl, $HClO_4$, and HNO_3 the c.t. species are the uranyl and protonated oxide ions of the lattice, while in H_2SO_4 sulphatouranate complexes are also involved. In carbonate solution the dicarbonatouranate ion and the protonated oxide ion are the c.t. species. The β-UO_3 dissolution reactions are interesting examples of c.t. kinetics since the oxide anions and uranyl cations of the β-UO_3 lattice form complexes with the cations and anions in the solutions in the process of dissolution and these complex-formation reactions are mirrored in the rate expressions for dissolution.

SEVERAL inorganic oxides dissolve non-oxidatively in acid or alkali solutions. That is, no change occurs in the formal oxidation states of the lattice constituents as they pass into solution. Rates of mass transport often determine the rates at which such oxides dissolve in aqueous solutions. However, preliminary experiments at the National Institute for Metallurgy, Johannesburg, suggested that the rates of dissolution of β-UO_3 † in both acid and carbonate solutions were not diffusion limited.
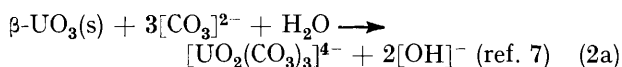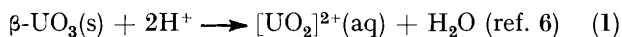
The kinetics of UO_3 dissolution in both acid and carbonate solutions have usually been determined as an afterthought in rate studies of the oxidative dissolution of UO_2. In the course of a study of the dissolution of UO_2 in carbonate solutions, Schortmann and De Sesa [1] quoted an activation energy of 14.3 kcal mol^{-1} and a first-order dependence on carbonate-ion concentration for the rate of UO_3 dissolution in carbonate solutions.‡ In a study concerned primarily with the dissolution

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† Uranium trioxide exists in six crystallographic modifications designated α, β, γ, δ, ε, and ξ as well as in an amorphous form.

‡ Throughout this paper: 1 cal = 4.184 J.

[1] W. E. Schortmann and M. A. De Sesa, *Proc. U.N. Internat. Conf. Peaceful Uses of Atomic Energy*, 1958, **3**, 333.

kinetics of UO_2 in HNO_3, Fillipov and Strelkov [2] include the observation that UO_3 dissolves more rapidly in HNO_3 than UO_2.

Kanevskii *et al.*[3] used UO_3 dissolution in H_2SO_4 to describe a new technique for dissolution rate measurements. These workers found that the rate of UO_3 dissolution in H_2SO_4 was limited by the diffusion of hydrogen ions to the UO_3 surface and/or a surface reaction, the relative importance of each rate-limiting process depending on the acid concentration and the velocity of the H_2SO_4 solution relative to the solid UO_3 surface. Gromov and Medvedev [4] stated that a mixture of various crystallographic forms of UO_3 dissolved in $0.1N$ H_2SO_4 at a rate which was not governed by mass-transport processes. These workers were, however, mainly concerned with the effect on the dissolution rate of γ-, β-, and neutron irradiation of the UO_3 particles. Cordfunke and van der Giessen [5] compared the rates (defined as the amount of $[UO_2]^{2+}$ in solution after 5 min) of dissolution of various crystallographic forms of UO_3 (α, β, γ, and ε) in HNO_3 over the range 1—10 mol dm^{-3} HNO_3. These crude rate data were obtained only to illustrate that the B.E.T. surface areas per unit mass of the various types of UO_3 were not the prime factors influencing the dissolution rate.

None of the above investigations represents a detailed kinetic or mechanistic study of UO_3 dissolution reactions in acid or carbonate solutions and this is one of the reasons for embarking on the present kinetic study. Another point of interest is that β-UO_3 dissolves in acid solutions by diprotonation of the oxide anion to yield water, and in carbonate solutions both by complexation of the uranyl ion with carbonate to form the tricarbonato-dioxouranate(vi) ion and protonation of the oxide anion to form the hydroxide ion [equations (1) and (2)].

$$\beta\text{-}UO_3(s) + 2H^+ \longrightarrow [UO_2]^{2+}(aq) + H_2O \quad (\text{ref. } 6) \quad (1)$$

$$\beta\text{-}UO_3(s) + 3[CO_3]^{2-} + H_2O \longrightarrow$$
$$[UO_2(CO_3)_3]^{4-} + 2[OH]^- \quad (\text{ref. } 7) \quad (2a)$$

$$2[OH]^- + 2[HCO_3]^- \rightleftharpoons 2[CO_3]^{2-} + 2H_2O \quad (2b)$$

Engell [8] and Vermilyea [9] have shown that several metallic oxides dissolve in acids at rates governed by the transfer of the lattice ions across the electrochemical-potential barrier at the solid–solution phase boundary, *i.e. via* a ' charge-transfer ' (c.t.) mechanism. Vetter [10] stated that a necessary condition for the c.t. mechanism is that the rate of dissolution should vary as a function of an externally applied potential across the solid–solution

phase boundary, *i.e.* the electrical double layer. Engell's theory of c.t. dissolution shows that the dissolution rate may be independent of a change in applied potential at the solid–solution phase boundary, while Vermilyea argues that the capacitance of a surface of an ionic solid is so large that relatively large changes in applied potential will cause only small changes in the electrical double-layer potential. Vermilyea further argues that the adsorption of ions of the electrolyte on the surface of the ionic solids is the only means of effectively achieving a change in potential across the electrical double layer.

In this paper it will be argued that the kinetics of dissolution of β-UO_3 in acid and carbonate solutions constitute a good example of the c.t. mechanism since both the uranyl and oxide ions of the β-UO_3 lattice can undergo adsorption reactions during dissolution.

EXPERIMENTAL

Materials.—Ammonium uranates $UO_3 \cdot (2 - x)H_2O \cdot xNH_3$ decompose between 600 and 800 K to yield β-UO_3. Details concerning their preparation and complex nature are described by Birkill,[11] Cordfunke,[12,13] and Stuart and Whateley.[14] All the preparations of β-UO_3 from ammonium uranate were carried out in a tube furnace flushed with air and programmed to follow a set temperature profile. By calcining the β-UO_3 products for either 4 or 100 h, by varying the calcination temperature between 673 and 783 K and by using different precursors, a series of β-UO_3 samples of differing crystallinity and specific surface area (12—28 m^2 g^{-1}) were prepared.[5,11] *X*-Ray diffraction patterns and i.r. spectra were used to identify the products as β-UO_3.

All the reagents were reagent grade. Doubly distilled water was used to make up all the solutions. The acid and carbonate solutions were standardised by potentiometric titration.

Apparatus and Method.—Two methods were used to study the rates of dissolution of β-UO_3 in acid and carbonate solutions. In the first method a β-UO_3 sample (*ca.* 5 mg) was dissolved in the solution (25 cm^3) and the rate of appearance of $[UO_2]^{2+}$ in solution was monitored by recording the current due to the reduction of U^{VI} at a gold rotating-disc electrode (r.d.e.). The apparatus used and the method are described by Nicol and Needes.[15]

The second method involves recording the temperature–time profile of the dissolution reaction of β-UO_3 (*ca.* 0.5 g) in a solution (400 cm^3) contained in a Dewar flask. This technique has been described in detail by Scott *et al.*[16]

RESULTS

Identical rate data were obtained from each measurement technique under identical conditions of β-UO_3 dis-

[2] A. P. Fillipov and L. A. Strelkov, *Radiokhimiya*, 1973, **15**, 186.

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[9] D. A. Vermilyea, *J. Electrochem. Soc.*, 1966, **113**, 1067.

[10] K. J. Vetter, ' Electrochemical Kinetics—Theoretical and Experimental Aspects,' Academic Press, New York, 1967.

[11] R. S. Birkill, Ph.D. Thesis, University of the Witwatersrand, Johannesburg, 1972.

[12] E. H. P. Cordfunke, *J. Inorg. Nuclear Chem.*, 1962, **24**, 303.

[13] E. H. P. Cordfunke, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3129.

[14] W. I. Stuart and T. L. Whateley, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1639.

[15] M. J. Nicol and C. R. S. Needes, A.E.B.(S.A.) Report PIN–171, 1973.

[16] P. D. Scott, D. F. Williams, and D. Glasser, *S. African J. Sci.*, 1974, **70**, 10.

solution in acid and carbonate solutions. The data were reduced to a dimensionless form: α = extent of dissolution (fraction of β-UO_3 dissolved) in time t, $t^* = t/t_{0.5}$, and $t_{0.5}$ = time at which $\alpha = 0.5$.
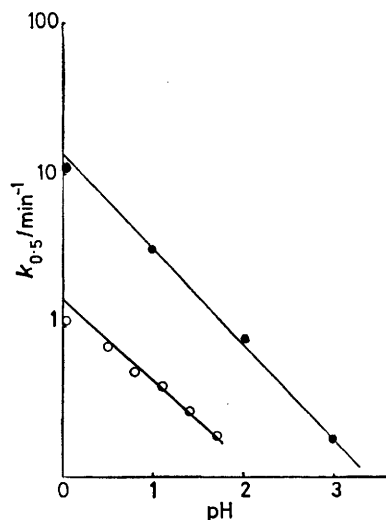

FIGURE 1 Plots of log $k_{0.5}$ against pH for the dissolution of β-UO_3 (type 16) in 1 mol dm^{-3} Na[ClO_4] ($\bullet$), and β-UO_3 (type 9) in $HClO_4$ ($\bigcirc$)

Various β-UO_3 samples were dissolved in solutions of different hydrogen- and carbonate-ion concentrations, containing different cation and anion types, at different temperatures and stirred at different speeds. All these experiments yielded, within experimental error, identical plots of α against t^*. This implies that the kinetic effects of the various parameters on the β-UO_3 dissolution rate need not be compared in terms of complete curves of dissolution extent against time. Rather, they may be compared by the use of the characteristic moment of each curve. Thus, one may define a 'half-life' constant for each dissolution rate measurement, namely $k_{0.5} = 1/t_{0.5}$
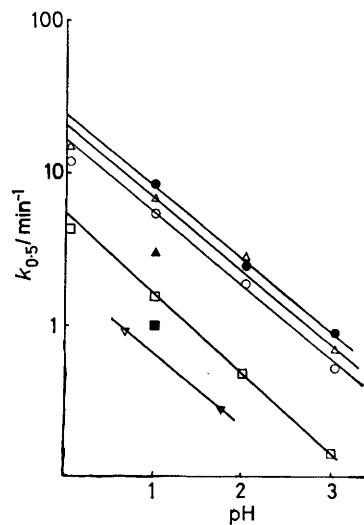

FIGURE 2 Plots of log $k_{0.5}$ against pH for the dissolution of β-UO_3 (type 16) in solutions of various sulphate salts (0.5 mol dm^{-3} M_n[SO_4]): ($\bullet$) Mg^{2+}, ($\triangle$) Li^+, ($\bigcirc$) Na^+, ($\blacktriangle$) [NH_4]$^+$, ($\square$) K^+, ($\blacksquare$) Cs^+, ($\triangledown$) β-UO_3 (type 13) in H_2SO_4 alone

Stirring.—In both the temperature monitoring and r.d.e. apparatus, minimum stirring speeds high enough to keep the β-UO_3 particles in suspension were always maintained. Variations in stirring speed over a wide range had no affect on the half-life constants or on the shapes of the curves of α against t^* for dissolution in both acid and carbonate solutions.

Rate as a Function of Hydrogen-ion Concentration.— Figures 1 and 2 are plots of the 'half-life' constants for β-UO_3 dissolution in acid solutions containing perchlorate or sulphate anions and the cations H$^+$, Mg^{2+}, Li$^+$, Na$^+$, [NH_4]$^+$, K$^+$, or Cs$^+$. The important features of these results are that the rates of dissolution are: (*i*) dependent approximately on the 0.5 order of [H$^+$] in all the solutions; (*ii*) at pH 0—0.5, weaker functions of [H$^+$] than those over the range 0.5—3; and (*iii*) inhibited by the presence of the various cations, the 'half-life' constants for dissolution following the order $Mg^{2+} \geqslant Li^+ > Na^+ > $ [NH_4]$^+ > K^+ > $ Cs$^+$.
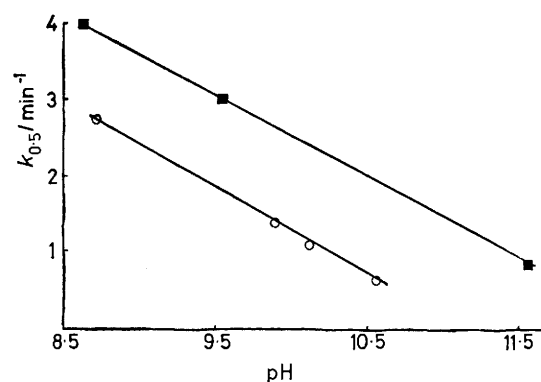
Figure 3 is a plot of the 'half-life' constants for β-UO_3

FIGURE 3 Plots of $k_{0.5}$ against pH for β-UO_3 dissolution in sodium carbonate solutions ([CO_3]$_T$ = 1.0 mol dm^{-3}) at 350 K: ($\blacksquare$) type 4, ($\bigcirc$) type 10

dissolution in carbonate solutions of various pH. The rates of dissolution decrease linearly with increasing pH, but are considerably weaker functions of pH than the 'half-life' constants for dissolution in acid solutions. Extrapolation of some of the lines in Figure 3 suggests that dissolution can be inhibited at high pH. These predictions are in fact fulfilled, in that under certain conditions some β-UO_3 samples do not dissolve or only dissolve incompletely.

Rate as a Function of Carbonate-ion Concentration.—The rates of β-UO_3 dissolution in sodium carbonate solutions of different total [CO_3^{2-}] were measured at 350 K. Carbonate to hydrogencarbonate concentration ratios in these solutions were kept constant. Figure 4 shows that a plot of the 'half-life' constants for dissolution against the total carbonate concentration is first order in [CO_3]$_T$.

Rate in Relation to Anion Type.—The rates of dissolution of two types of β-UO_3 (types 11 and 13) in solutions of perchloric, nitric, hydrochloric, and sulphuric acids at 278 K were recorded. The relevant 'half-life' constants are in the Table. These data show that β-UO_3 dissolved at almost equivalent rates in solutions of $HClO_4$, HNO_3, and HCl, but in a comparable solution of H_2SO_4 the rate virtually doubled. No additional anions were added to the carbonate solutions.

Rate Dependence on Cation Type.—Relative rates of β-UO_3 dissolution at pH 1 in solutions containing various

cations are plotted in Figure 5 as a function of the ionic radii and the hydration energies of the various cations.
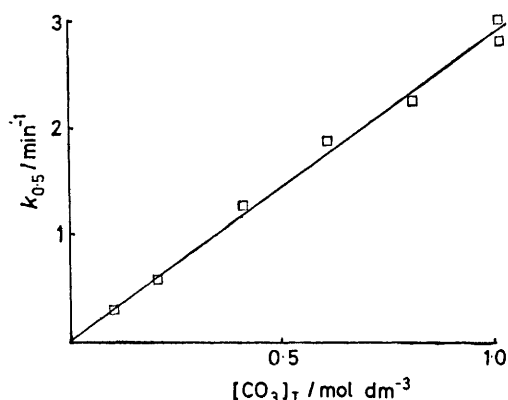

FIGURE 4 Plot of $k_{0.5}$ against total carbonate concentration, $[CO_3]_T$, for β-UO_3 (type 4) dissolving in $Na[HCO_3]$–$Na_2[CO_3]$ solutions at 350 K

The 'half-life' constants decrease with increasing ionic radius and increase with increasing hydration energy.

$k_{0.5}$ in relation to acid co-anion for two different preparations of β-UO_3 designated types 11 and 13 at 278 K

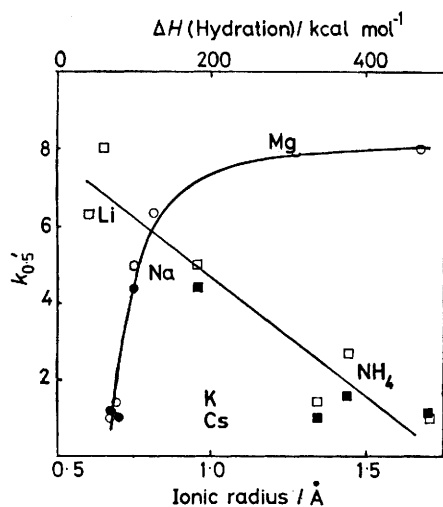| β-UO_3 type	Aqueous acid	$\dfrac{[H^+]}{mol\ dm^{-3}}$	$\dfrac{k_{0.5}}{min^{-1}}$	$\dfrac{\Delta H\ (\text{dissolution})}{kcal\ mol^{-1}}$
	$HClO_4$	0.0536	1.16	18.91
	HCl	0.053 6	1.18	17.82
11	HCl	0.053 6	1.19	18.96
	HNO_3	0.053 6	1.33	17.45
	0.027 mol dm^{-3} H_2SO_4	0.041	3.12	19.68
13	$HClO_4$	0.32	0.458	19.10
	$HClO_4$	0.32	0.471	17.92
	HCl	0.32	0.451	19.08
	HCl	0.32	0.500	18.69
	HNO_3	0.32	0.441	19.44
	0.16 mol dm^{-3} H_2SO_4		0.970	18.45

FIGURE 5 Plots of $k_{0.5}'$ (the ratio of the rate of dissolution to the lowest dissolution rate) against the ionic radius and the hydration energy of the cations: (●) and (■) dissolution in carbonate solutions; (□) and (○) dissolution in acid solutions. Squares represent ionic radius and circles hydration energy

The rates of dissolution of β-UO_3 in carbonate solutions containing one of a set of co-cation types were measured under similar conditions of carbonate concentration, pH, and temperature. The relative dissolution rates, which are also recorded in Figure 5 for comparison with the results in acid solutions, displayed a strong dependence on co-cation type, with $Na^+ > [NH_4]^+ > Cs^+ \geqslant K^+$. Furthermore, the variations in dissolution rates as a function of cation type are very similar in both acid and carbonate solutions.
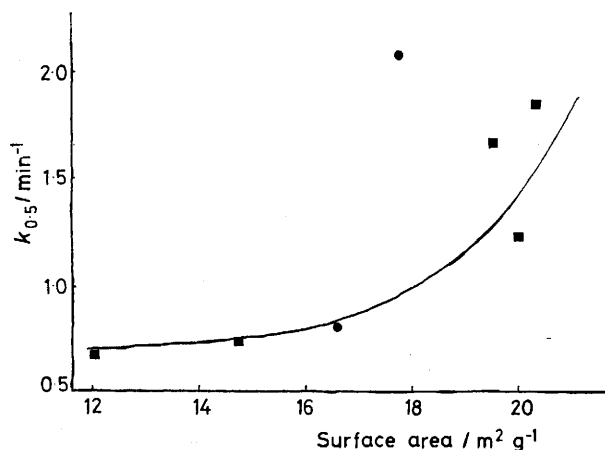

FIGURE 6 Plot of $k_{0.5}$ against surface area for the dissolution of β-UO_3 (types 3, 4, 7, 8, 9, 12, and 15) in sodium carbonate solutions ($[CO_3]_T = 0.6$ mol dm^{-3}) at 350 K and pH 9.6. Calcination time: (●) 4, (■) 100 h. Calcination temperature: types 3 and 7, 673; 4, 9, and 15, 723; 12, 743, and 8, 783 K
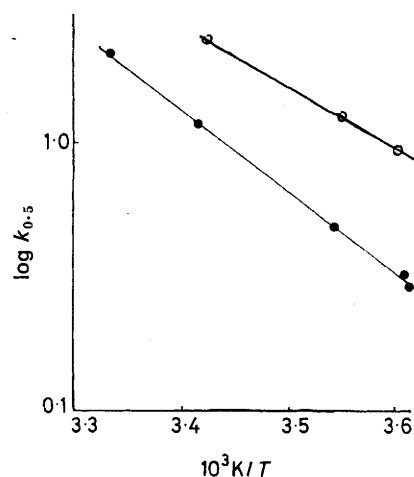

FIGURE 7 Plots of log $k_{0.5}$ against $1/T$ for β-UO_3 (type 9) dissolution in acid solution: (●) 0.32 mol dm^{-3} $HClO_4$, HCl, or HNO_3; (○) 0.16 mol dm^{-3} H_2SO_4

Rate as a Function of the Properties of β-UO_3.—Various types of β-UO_3 samples, with different specific surface areas, preparative histories, or uranate precursors were dissolved in carbonate solutions under identical experimental conditions and the rates of dissolution were measured. The results are depicted in Figure 6 which is a plot of the $k_{0.5}$ values for dissolution against the specific surface areas of the various samples. This graph reveals that the rate of β-UO_3 dissolution is not a unique function of the specific surface area of the β-UO_3 but depends on calcination time or temperature.

Only a few types of β-UO_3 were used to study the dissolution kinetics of β-UO_3 in acid solutions, and the kinetic effects of the properties of the β-UO_3 samples are identical to those for β-UO_3 dissolution in carbonate solutions.
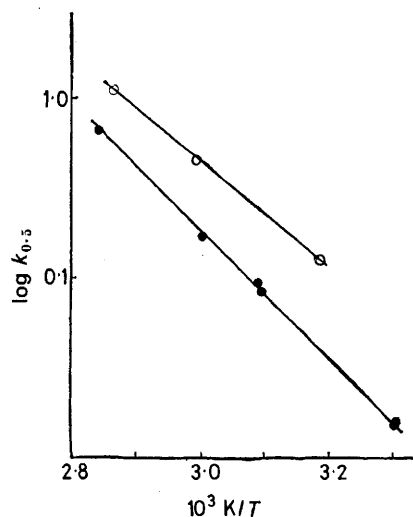
Rate as a Function of Temperature.—Figures 7 and 8

FIGURE 8 Plots of log $k_{0.5}$ against $1/T$ for β-UO_3 (type 9) dissolution in carbonate solutions: ($\bullet$) 0.3 mol dm^{-3} Na-[HCO_3] + 0.3 mol dm^{-3} Na$_2$[CO_3] at pH 9.6; (○) 0.6 mol dm^{-3} Na[HCO_3] at pH 8.5
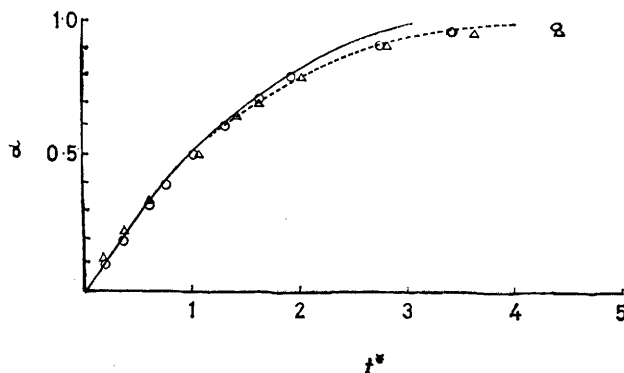

FIGURE 9 Curves of α against t^* for the dissolution of β-UO_3 samples of extremes of preparative temperature, surface area, and precursor type in acid and carbonate solutions: ($\triangle$) type 11 (100-h calcination at 683 K, surface area = 27.7 m^2 g^{-1}; precursor R-A.U.) in 0.32 mol dm^{-3} HClO$_4$ at 278 K; (○) type 13 (100-h calcination at 783 K, surface area = 12.0 m^2 g^{-1}, precursor D-A.U.) in 0.3 mol dm^{-3} Na[HCO_3] + 0.3 mol dm^{-3} Na$_2$[CO_3] at 350 K; (————) $R_2(\alpha) = 1 - (1 - \alpha)^{\frac{1}{2}} = kt/r$; (——) $R_3(\alpha) = 1 - (1 - \alpha)^{\frac{1}{3}} = kt/r$

contain plots of log $k_{0.5}$ against $1/T$ for β-UO_3 dissolution in acid and carbonate solutions, respectively. The important features of these results are: (i) the activation energies for dissolution in HClO$_4$, HCl, and HNO$_3$ were similar and were of the order of 14 kcal mol^{-1}, while the activation energy for dissolution in H$_2$SO$_4$ was ca. 10 kcal mol^{-1}; (ii) the activation energy for dissolution in carbonate solutions increased with increasing pH, values of 14.5 kcal mol^{-1} at pH 8.5 and 16.0 kcal mol^{-1} at pH 9.6 being obtained (cf. 14.3 kcal mol^{-1}).

[17] H. O'Hashi and T. Morozumi, *Nippon Genshiryoku*, 1967, **9**, 65.
[18] S. Arhland and L. Brandt, *Acta Chem. Scand.*, 1968, **22**, 1579.

Heats of Dissolution.—The temperature technique yields the heat of each dissolution reaction as well as the rate. Uranyl ions form very weak complexes with chloride, nitrate, and perchlorate anions,[17] and fairly strong mono- and di-sulphato-complexes (but the heats of formation are small compared to the heats of dissolution).[18]

Values of the heat of reaction (1) obtained in this work varied between -17.2 and -19.1 kcal mol^{-1}. Cordfunke and van der Giessen [5] gave values between -17.8 and -18.5 kcal mol^{-1} (the less crystalline the β-UO_3 sample, the more exothermic the value) for β-UO_3 dissolution in 6 mol dm^{-3} HNO$_3$ at 298 K. Values of the heats of dissolution of the various β-UO_3 samples in carbonate solutions were also calculated. In all the carbonate solutions except ammonium carbonate solution, these heats of dissolution correspond to the enthalpies of the dissolution reaction followed by a neutralisation reaction [(2a) followed by (2b) ($2\Delta H^{\ominus} = -19.60$ kcal mol^{-1}) [19]]. Values of 18—21 kcal mol^{-1} were obtained for the heats of dissolution of various β-UO_3 samples in carbonate solutions of pH 9.6.

DISCUSSION

The fact that identical curves of α against t^* are obtained from the two methods of kinetic analysis is significant. The r.d.e. measures the rate of appearance of the final product, while the temperature method measures the total heat generated in all the steps up to that time. This result strongly suggests there is only one major rate-limiting step in the dissolution reaction.

A sequence of four possible rate-controlling processes occurs when a solid dissolves in an electrolyte solution, namely crystallisation, reaction, charge transfer, and diffusion.[10] Crystallisation involves the conversion of the bulk-lattice constituents into adsorbed surface species called ad-atoms or ad-ions.[20] Clearly the rate of such a partial process would not depend on solution parameters, so that the rate of dissolution of β-UO_3 cannot be wholly determined by the crystallisation step. Consequently the crystallisation step will be assumed to be in a state of pseudo-equilibrium during the dissolution of β-UO_3 in acid and carbonate solutions.

It is possible that the rates of β-UO_3 dissolution are mass-transport controlled, but are only very weak functions of impeller rotation speed.[21] However, both the shapes of the curves of α against t^* and the 'half-life' constants for dissolution of α-uranium trioxide dihydrate (α-$UO_3 \cdot 2H_2O$) in acid solutions are strong functions of stirrer speed. The α-$UO_3 \cdot 2H_2O$ sample studied was prepared by hydration of β-UO_3 (type 13) in water at 350 K. Both the β-UO_3 and α-$UO_3 \cdot 2H_2O$ particles have similar size distributions, shapes, and densities. Consequently, the observation that β-UO_3 dissolution rates are unaffected by stirring while α-$UO_3 \cdot 2H_2O$ dissolution rates are strongly affected suggests that the rate of β-UO_3 dissolution in acid

[19] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, Selected Values of Chemical Thermodynamic Properties, N.B.S.(U.S.) Technical Note 270–3, 1968.
[20] W. Lorenz, *Z. phys. Chem.*, 1953, **202**, 275.
[21] Z. Štěrbáček and P. Tausk, 'Mixing in the Chemical Industry,' 1st English edn., Pergamon, Oxford, 1965, vol. 5.

solutions is not mass-transport limited. Several other kinetic observations such as the fractional order in [H⁺], the cation effects, and the high activation energy also exclude this possibility.

The observed kinetic data for β-UO_3 dissolution in acid solutions can be modelled by the c.t. theory. This is a general theory of heterogeneous solid-electrolyte solution reaction which describes the rate of transfer of the lattice cations and anions of the solid across the electrochemical-potential barrier at the solid–solution phase boundary. Equations which describe the rate at which β-UO_3 dissolves in acid and carbonate solutions under c.t. rate control are simply deduced from those given by Vetter.[10] Equations (3a) and (3b), which are an appropriate form of the Butler–Volmer equation which describes the rate of electron-transfer processes at electrodes, can be written for protonated oxide and carbonatouranate c.t. ions from a β-UO_3 lattice. The

$$v_U = \overrightarrow{k}_+[U_{ad}][CO_3]_T{}^{n-m}\exp(\alpha_+ z_+ FE/RT)$$
$$-\overleftarrow{k}_+[U(CO_3)_n][CO_3]_T{}^{-m}\exp[-(1-\alpha_+)z_+ FE/RT] \quad (3a)$$

$$v_O = \overrightarrow{k}_-[O_{ad}][H^+]^{s-t}\exp(\alpha_- z_- FE/RT) -$$
$$-\overleftarrow{k}_-[OH_s][H^+]^{-t}\exp[-(1-\alpha_-)z_- FE/RT] \quad (3b)$$

symbols used are defined as follows: v_U and v_O = rates of charge transfer of the uranyl and oxide species; $[U_{ad}]$ and $[O_{ad}]$ = concentrations of the uranyl and oxide ad-ions; $[U(CO_3)_n]$ ($n = 1$—3), [OH], [H⁺], and $[CO_3]_T$ = concentrations of the carbonatouranate, hydroxide, hydrogen, and total carbonate ions $[CO_3]^{2-}$ + $[HCO_3]^-$ in solution; $\overrightarrow{k}_+, \overleftarrow{k}_+, \overrightarrow{k}_-$, and $\overleftarrow{k}_-$ = forward and reverse rate constants for the lattice cation and anion c.t. reactions; α_+ and α_- = transfer coefficients for the lattice cations and anions; z_+ and z_- = charges on the lattice cations and anions; and E = the electrical potential difference between the β-UO_3 surface and the outer Helmholtz plane (o.h.p.). In writing the equations in this form it has been assumed that in acid solutions (where $[CO_3]_T = 0$) the co-anions of the acids are not involved in the c.t. process. This assumption probably holds for perchlorate, nitrate, and chloride ions since these do not complex with uranyl ions to any significant extent in homogeneous solution.[17] However, fairly strong sulphatouranate complexes form in homogeneous solution and the appropriate c.t. expression under these conditions will be discussed later.

In the steady state, $v_U = v_O$. The potential across the β-UO_3 solution phase boundary was not potentiostatically controlled in this work. In these circumstances, Vermilyea[9] suggested that the rates of the deposition reactions in equations (3a) and (3b) be neglected and that $v_U = v_O$ be used to eliminate E from the rate expression. One thus obtains (4), where

$$v = v_U = \overrightarrow{k}_+[U_{ad}][CO_3]_T{}^{n-m}(\overrightarrow{k}_-[O_{ad}][H^+]^{s-t}/$$
$$\overrightarrow{k}_+[U_{ad}][CO_3]_T{}^{n-m})^x \quad (4)$$

$x = \alpha_+ z_+/(\alpha_+ z_+ - \alpha_- z_-)$. According to Vermilyea,

equation (4) may be applied in a number of different ways to explain the 0.5—0.6-order dependences of the rates on [H⁺] during β-UO_3 dissolution in acid solutions ($[CO_3]_T = 0$). The oxide ad-ions may form hydroxide ions with the hydrogen ions, two hydrogen ions may react with oxide ad-ions to form water, or hydrogen ions may be chemisorbed to form a saturated layer of surface hydroxyl groups. By suitable and not unreasonable choice of the transmission coefficients the required order is obtained. The hydration of the β-UO_3 surface to form hydroxide ions, as with MgO in acid solutions,[22] is excluded by the fact that the rate of dissolution of β-$UO_3\cdot2H_2O$ in acid solution is rate-limited by mass transport.

At pH 0—1 the kinetic order in [H⁺] decreases rapidly. This observation can be explained in terms of the saturation of adsorption sites on the β-UO_3 surface. An analysis of the extent of saturation using an experimental theory of adsorption at oxide surfaces due to Parks[23] gives a value of pH -0.2 for the point of zero charge (p.z.c.) of β-UO_3. This result is derived as follows. Suppose adsorption of protons on a negative oxide ad-ion site to form a positively charged surface site occurs in accordance with reaction (5). The stability

$$O^-_{ad} + 2H^+ \rightleftharpoons [OH_2]^+_{ad} \quad (5)$$
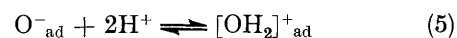
constant K_H for this reaction is given by (6). At the

$$K_H = \frac{[OH_2{}^+_{ad}]}{([O^-_{ad}] - [OH_2{}^+_{ad}])[H^+]^2} \quad (6)$$

p.z.c., $[OH_2{}^+_{ad}] = [O^-_{ad}] - [OH_2{}^+_{ad}]$ and $2pH = -pK_H$.

The rate of dissolution at pH 0 is $ca.$ 30% lower than that predicted by the extrapolation of the straight line in Figure 1. Assuming that the decrease in rate is due to a 30% decrease in original O_{ad} sites one obtains $K_H = 0.5$ dm³ mol⁻¹ from equation (4) and hence a p.z.c. of pH -0.2. Although the p.z.c. of UO_3 has not been measured as far as we are aware, Parks[23] estimated a p.z.c. of pH -0.7 on the basis of a simplified crystal-field theory.

Equation (3) does not predict the linear dependence on pH of the dissolution rate in carbonate solutions. It has been estimated that even for $[CO_3]_T = 0.1$ mol dm⁻³ and $[U(CO_3)_3] = 0.01$ mol dm⁻³, $i.e.$ the closest approach to equilibrium in this work, the reactions described by equations (3a) and (3b) will only be in equilibrium for [OH] = 300 mol dm⁻³. However, consideration of the solubility product of $UO_3\cdot2H_2O$ ($\simeq 10^{-22}$ mol² dm⁻⁶)[5] and the stability constant of the tricarbonatouranate ion (10^{-22} mol³ dm⁻⁹)[5] indicates that for $[CO_3]_T = 0.1$ mol dm⁻³ and $[U(CO_3)_3] = 0.01$ mol dm⁻³ equilibrium is reached at [OH] = 0.1 mol dm⁻³. Consequently, a more detailed description of the c.t. processes which occur must include the c.t. equations of hydroxide-ion deposition. Such equations do not, in general, yield simple

[22] D. A. Vermilyea, $J.$ $Electrochem.$ $Soc.$, 1969, **116**, 1179.
[23] G. A. Parks, $Chem.$ $Rev.$, 1965, **65**, 177.

solutions for E so that the rate of dissolution cannot be expressed in a form analogous to equation (4).

The inhibition of the dissolution of β-UO$_3$ at high pH and at high co-cation concentrations may be ascribed to the precipitation of insoluble uranyl complexes on the surfaces of the UO$_3$ particles. The solubility products of both the uranates [25,26] and the tricarbonatouranate salts [24] of sodium and potassium ions are sufficiently low to cause precipitation under the experimental conditions used in this work.

Rate Dependence on Carbonate Ion.—Uranyl mono-carbonate, [UO$_2$][CO$_3$], is insoluble and a sample prepared * from β-UO$_3$ dissolves more rapidly in carbonate solutions than its precursor, so that the rate of dissolution of a carbonated surface of UO$_3$ is unlikely to be the rate-determining step of β-UO$_3$ dissolution in carbonate solutions.

If the dicarbonatouranate ion is the c.t. species then $n = 3$, $m = 1$ in equation (4) and $\alpha_+ = \alpha_-$ is the relation required to predict the linear dependence of dissolution rate on total carbonate concentration. If the tricarbonatouranate ion is the c.t. species $n = 3$, $m = 0$ in equation (4) and $\alpha_+ = 2\alpha_-$.

Rate Dependence on Cation Type.—The depression of the β-UO$_3$ dissolution rate in acid and carbonate solutions by cations may be explained in terms of the blocking of reactive oxide ad-ion dissolution sites by adsorbed cations. Such a mechanism requires the dehydrated cation to be adsorbed in the i.h.p.[27] In terms of Parks theory of such adsorption processes the cations with large charge-to-radius ratios should be most strongly adsorbed. However, the same cations may be expected to be most strongly hydrated. Since specific adsorption in the i.h.p. involves dehydrated or partially dehydrated cations, the relative strength of adsorption of the various cations will be determined by the opposing energies of adsorption and dehydration of the cations. In the case of β-UO$_3$ it appears that the dehydration energies of the cations rather than the adsorption energies determine the relative strengths of cation adsorption on a β-UO$_3$ surface, *i.e.* the more strongly hydrated the cation the more weakly it will be adsorbed on the β-UO$_3$ surface. A similar explanation has been offered by Hallaba *et al.*[28] to explain the relative strength of adsorption of cations on hydrated zirconia. Strong adsorption of cations in the i.h.p. of β-UO$_3$ may be expected to appreciably alter the potential difference across the e.d.l. However, the modified value of E does not appear explicitly in the dissolution rate expression [equation (3)] but is accounted for by replacing O$_{ad}$ by O$'_{ad}$, the reduced number of oxide ad-anion sites.

Rate Dependence on Anion Type.—The finding that sulphate ions enhance the rate of dissolution of β-UO$_3$

in acid solutions, while perchlorate, nitrate, and chloride ions exert no effect, may be ascribed to complexing of sulphate with uranyl ad-cations. Such behaviour may be correlated qualitatively with the complexing reactions of the uranyl ion in solution. Since sulphatouranate complexes are not very strongly complexed relative to the di- and tri-carbonatouranates, for example, it is unlikely that the sulphatouranates are the only species involved in the c.t. process of the uranyl ion, *i.e.* the charge transfer of the bare uranyl ion will probably also contribute to the rate of dissolution. Under these conditions equation (3a) becomes (3c) if one assumes

$$v_U = \vec{k}_+[U_{ad}]\exp(\alpha_+ z_+ FE/RT) +$$
$$\vec{k}_+{}'[U_{ad}][SO_4]^p\exp(\alpha_+ z_+ FE/RT) \quad (3c)$$

that the deposition reactions may be neglected. Equation (3c) combined with equation (3b) in the steady state yields (7), where $x = \alpha_+ z_+/(\alpha_+ z_+ - \alpha_- z_-)$. Equation (7)

$$v = v_U = [U_{ad}](\vec{k}_+ + \vec{k}_+{}'[SO_4]^p)\{\vec{k}_-[O_{ad}][H^+]^{s-t}/$$
$$[U_{ad}](\vec{k}_+ + \vec{k}_+{}'[SO_4]^p)\}^x \quad (7)$$

can by a suitable choice of p and the relative values of $\vec{k}_+$ and $\vec{k}_+{}'$ predict the observed increase in dissolution rate in the presence of sulphate ion without in any way changing the predicted rate dependence on [H$^+$].

Rate as a Function of the Nature and Properties of β-UO$_3$.—As shown in Figure 9 the curves of α against t^* for β-UO$_3$ dissolution are similar to the theoretical curves for reaction occurring on the surface of a sphere which shrinks with time [$R_3(\alpha)$] or reaction occurring at the edge of a disc which shrinks radially with time [$R_2(\alpha)$].† β-Uranium trioxide occurs as spherical agglomerates of disc-shaped crystallites.[11] The experimental curves of α against t^* have shorter tails than the $R_3(\alpha)$ plots. Were $R_3(\alpha)$ the correct model the reverse would be expected of the distribution of particle sizes that occurred in the β-UO$_3$ samples used in this work. Therefore it seems that dissolution occurs at the edges of the disc-shaped β-UO$_3$ crystallites but not at the plane surfaces of the discs. This is a reasonable postulate since the plane surfaces of the β-UO$_3$ crystallites are composed of uranyl oxygen atoms, which remain bonded to the uranium atoms during dissolution. However, the edges of the β-UO$_3$ crystallite discs comprise uranium–oxygen bonds which are broken during dissolution.[29]

The variation of the β-UO$_3$ dissolution rates as a function of the preparative histories of the various sample types can be explained by postulating that the rate of dissolution decreases with increasing crystallinity of the β-UO$_3$ samples. β-Uranium trioxide is a poorly crystalline phase. Its structure and degree of crystallinity are isomorphous to the corresponding properties of

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* By bubbling CO$_2$ through a suspension of β-UO$_3$ particles in water.
† The functions $R_2(\alpha)$ and $R_3(\alpha)$ are defined in Figure 9.

[24] L. G. Sillen, ' Stability Constants of Metal–Ion Complexes,' *Special Publ.*, The Chemical Society, London, 1965, no. 17.
[25] B. Tomazic and M. Branica, *Croat. Chem. Acta*, 1966, **38**, 249.

[26] V. Baran and M. Tympl, *J. Inorg. Nuclear Chem.*, 1966, **28**, 29.
[27] H. J. L. Wright and R. J. Hunter, *Austral. J. Chem.*, 1973, **26**, 1183.
[28] E. Hallaba, H. Z. Misak, and H. N. Salama, *Indian J. Chem.*, 1973, **11**, 580.
[29] P. C. Debets, *Acta Cryst.*, 1966, **21**, 589.

its ammonium uranate precursor.[5,11] Increasing calcination time and temperature improve the crystalline structure of β-UO_3.[11] As the crystallinity of the β-UO_3 samples improves so, it is proposed, the concentration of ad-ion dissolution sites on the edges of the β-UO_3 crystallite disc decreases, thus causing a reduction in dissolution rate in accordance with equations (4).