Kinetic Investigation of the Reaction between Tungsten and Bromine

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The reaction between tungsten and bromine has been studied between 1 063 and 1 213 K with bromine concentrations of 0·5—1·5 mol m^{-3} in a static system utilising a quartz spring to record weight loss. The reaction is zero order with respect to tungsten concentration, but the order with respect to bromine varies from 1·70 to 1·16 with increase in temperature. The species produced at the tungsten surface are probably WBr_2 and WBr_5 and their formation is attributed to stepwise attack by atomic bromine on the tungsten. The rate constant over the temperature range is given by $k/\text{mol}^{-\frac{1}{2}}\,\text{m}^{5/2}\,\text{s}^{-1} = 1{\cdot}12 \times 10^{-9} \exp - (82{\cdot}7 \pm 4{\cdot}0\ \text{kJ mol}^{-1}/RT)$. The effect of addition of argon and nitrogen on the reaction system has been studied. Reaction rates are in excess of those expected for simple dilution and this is partially explained on the basis that the increased rate is a consequence of traces of oxygen present in the two gases.

OVER the last decade a number of investigations have been reported on the kinetics of the tungsten–oxygen–halogen system. McKinley [1] undertook a mass-spectrometric investigation of the tungsten–oxygen–chlorine system below 10^{-5} Torr and Zubler,[2,3] using a microbalance flow system, studied the tungsten–oxygen–bromine system over the pressure ranges 10^{-4}—10^{-2} Torr oxygen and 0·3—2·7 Torr bromine.‡ The reaction between tungsten and halogens has been reported. Rosner and Allendorf studied the tungsten–fluorine [4] and molybdenum–chlorine [5] systems for both molecular and atomic halogen, but the only reported kinetic study for bromine is that between bromine and nickel.[6] The reaction between tungsten and bromine has been used to prepare WBr_5. Colton and Tomkin [7] reported that the reaction proceeded at a satisfactory rate at 773 K, but McCarley and Brown [8] reported that a temperature of 1 023 K was necessary. Our interest in the chemistry of tungsten–halogen incandescent lamps and the observations that these lamps function more efficiently when an oxygen getter is present [9] has motivated us to study the reaction between tungsten and bromine in the absence of oxygen.

The majority of the investigations outlined above involved low partial pressures of reactant species. In

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‡ 1 Torr = (101 325/760) Pa.

[1] J. D. McKinley, *Proc. Internat. Symp. Reactive Solids*, 1969, Wiley–Interscience, New York, 1969, pp. 345—351.

[2] E. G. Zubler, *J. Phys. Chem.*, 1970, **74**, 2479.

[3] E. G. Zubler, *J. Phys. Chem.*, 1972, **76**, 320.

[4] D. E. Rosner and H. D. Allendorf, *J. Phys. Chem.*, 1971, **75**, 308.

[5] D. E. Rosner and H. D. Allendorf, *J. Phys. Chem.*, 1965, **69**, 4290.

[6] J. D. McKinley, *J. Chem. Phys.*, 1964, **40**, 576.

[7] R. Colton and I. B. Tomkin, *Austral. J. Chem.*, 1966, **19**, 759.

[8] R. E. McCarley and T. M. Brown, *J. Amer. Chem. Soc.*, 1962, **84**, 3216.

[9] J. M. Rees, *Lighting Research and Technology*, 1970, **2**, 257.

cases where the effect of oxygen is considered this is not detrimental, but if the reaction between metal and halogen is to be studied and halide oxides are possible then it could have considerable effect on the reaction rate. In an effort to avoid these complications we have used high bromine concentrations, 0·5—1·5 mol m^{-3} (10—25 Torr), and in the majority of experiments bromine was the only gas present. In the tungsten–bromine system the participation of oxygen is readily indicated by the presence of orange WBr_2O_2 resulting from reaction (1). It has been reported[10] that the

$$W(s) + O_2(g) \longrightarrow WO_2(s) + Br_2(g) \longrightarrow WBr_2O_2(g) \quad (1)$$

reaction between tungsten and halogens is kinetically different in nitrogen and argon; consequently experiments were carried out using these two gases as ballast in an effort to elucidate the possible mechanism.

EXPERIMENTAL

The kinetic experiments were conducted in the static system shown in Figure 1. This consisted of a Pyrex reaction loop with a quartz-heated section (40 × 4 cm diameter) and a ballast vessel (A) (3 dm^3). The vessel (A) was included so that the bromine pressure remained constant throughout a kinetic run. No run represented more than a 2% reduction in pressure. To facilitate sample changing the loop was made demountable by the insertion of B34 and ball joints. The bromine pressure introduced into the loop was measured by the spiral manometer (B) which had a maximum sensitivity of 0·05 Torr. The tungsten sample was suspended by means of a quartz thread (40 cm long) from a quartz spiral spring (1 g capacity, Thermal Syndicate) into the central zone of the furnace. The furnace, which was controlled by a solid-state proportional controller, had a thermal stability of ±1 K at 1 213 K and a linear central zone of 10 cm to within ±1 K. The quartz spring had a maximum extension of 25 cm for a 1 g load and spring movement was measured by a cathetometer (Precision Tool and Instrument) with maximum sensitivity of 0·01 mm, thus allowing a weight loss of 40 µg to be detected. Calibration runs, with the loop filled with inert gas, showed that the spring was insensitive to temperature variations, consequently thermostatting of the spring was not necessary. The baffles (C) and (D), with a centre hole 1·5 cm in diameter, were introduced to reduce the thermal flow and prevent product condensing on the tube wall in the vicinity of the spring location point. Prior to commencement of kinetic runs the apparatus was flushed with dry nitrogen *via* tap (E), and evacuated to better than 10^{-3} Torr. The system was continuously pumped during warm-up.

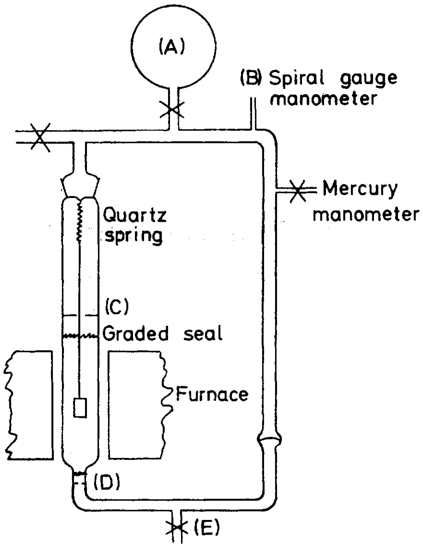

FIGURE 1 Diagram of static reaction system used in kinetic study

The kinetic runs involved introducing bromine into the loop at a known pressure and following the movement of the spring with the cathetometer. After the bromine had been introduced the system was allowed to equilibrate for a few minutes; this allowed bromine to be adsorbed on to the tungsten surface and any oxygen present to react with the tungsten to form WBr_2O_2. Readings were taken at various time intervals, runs requiring in the region of 1—3 h. At the end of a run the bromine was condensed out of the loop and the system was rechecked for vacuum. Normally there was no variation from the initial reading, but if there was a variation in excess of 10^{-2} Torr the run was disregarded. In runs with a mixture of Br_2 and an inert gas the desired concentration of bromine was introduced into the reaction loop first and inert gas was added until the total required pressure was obtained. A backing-off facility was added to the spiral manometer to enable pressures of 100 Torr to be used. Readings were taken only after sufficient time had been allowed for the gases to mix.

Electron micrographs were taken of the tungsten surface at various stages of reaction. An A.E.I. EM6 electron microscope was used and samples were prepared by the standard replica technique, with shading by gold–palladium alloy at 45°.

Materials.—Liquid bromine (B.D.H., 99·8%) was degassed, dried by distillation over phosphorus pentaoxide, and stored *in vacuo*. As an additional precaution the bromine was thoroughly degassed daily. The tungsten surface was in the form of 0·025 mm thick tungsten foil (Koch–Light, 99·9%) with a geometric area of 5·5 × 10^{-4}—6·0 × 10^{-4} m^2 and weighing *ca*. 250 mg. Surface preparation was originally carried out by heating under reflux with thionyl chloride, but it was subsequently found that simply degreasing with acetone was sufficient. In addition to cleaning, the sample was subjected to a conditioning run with 25 Torr Br_2 before kinetic measurements were begun. This treatment removed any adsorbed oxygen and also traces of surface impurity. The sample was replaced when its weight had decreased to *ca*. 20% of the original. No attempts were made to recrystallise the tungsten foil because the temperature region of interest in a tungsten halogen lamp would not be sufficiently high to allow the filament supports to recrystallise (>1 800 K). Both the nitrogen and argon used in the kinetic experiments were grade X purity (B.O.C.). The nitrogen was introduced from a cylinder *via* Nylon piping; the argon was in a soda-glass bottle directly attached to the line.

RESULTS

In all, five tungsten samples were used and gave reproducible results as can be seen from Table 1.

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[10] E. A. Mosby, L. J. Schupp, G. G. Steiner, and E. G. Zubler, *Light Sources*, 1966, **1**, 1.

TABLE 1

Reproducibility between various samples of tungsten foil

Sample	T/K	[Br_2]/mol m^{-3}	10^{-14}Rate/ mol m^{-2} s^{-1}
(A)	1 163	0·846	14·0
(B)	1 163	0·858	13·9
(A)	1 163	1·145	23·6
(C)	1 163	1·163	24·0
(A)	1 163	0·564	9·4
(D)	1 163	0·576	8·4
(A)	1 063	0·858	8·0
(E)	1 063	0·875	8·3

Bromine as Sole Gaseous Species.—Rate measurements above 10^{-14} mol m^{-2} s^{-1} were made at intervals from 1 063 to 1 213 K with bromine concentration in the range 0·5—1·5 mol m^{-3}. The weight loss of tungsten was linear with time at all temperatures and pressures of bromine; thus the reaction was zero order with respect to tungsten as would be expected for this system where there was an excess of tungsten available for reaction. The tungsten weight loss was found to be dependent on bromine concentration. The variation in weight loss with time for various bromine concentrations is shown in Figure 2. On plotting log (Rate) against log [Br_2], straight lines were obtained at all temperatures (Figure 3), the gradients of which showed a variation from 1·70 to 1·16 with increase in temperature. Thus the rate equation is V/mol m^{-2} s^{-1} = $k[W][Br_2]^n$ where n is between 1·70 and 1·16 depending on the temperature. A value for the rate constant was obtained at each temperature by extrapolating the plots in Figure 3 to unit bromine concentration. A least-squares analysis of a log k against $1/T$ plot gave expression (2) for the rate constant

$$k/\text{mol}^{-\frac{1}{2}}\,\text{m}^{5/2}\,\text{s}^{-1} = 1{\cdot}12 \times 10^{-9} \exp -(82{\cdot}7 \pm 4{\cdot}0/RT) \qquad (2)$$

between 1 063 and 1 213 K. The units of k are the result of assuming a mean order of 3/2 and $E^‡$ is in kJ mol^{-1}.

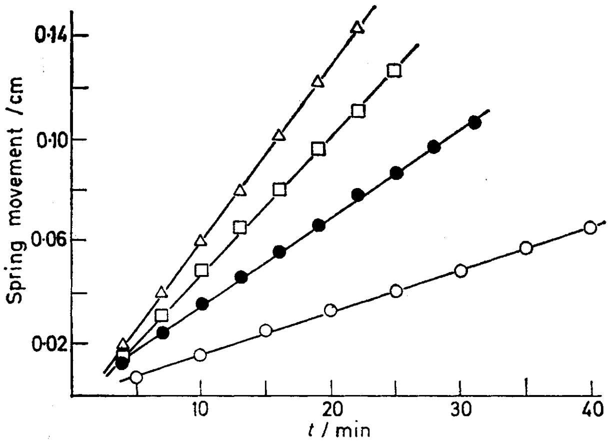

FIGURE 2 Loss in weight of tungsten foil with time at 1 113 K and [Br_2] = 0·587 (○), 0·880 (●), 1·174 (□), and 1·468 mol m^{-3} (△)

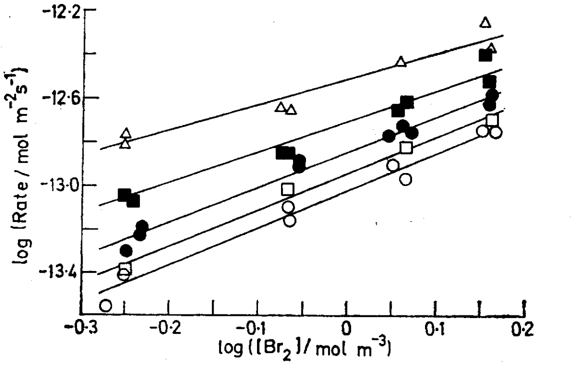

FIGURE 3 Variation of log (Rate) with log [Br_2] at 1 063 (n = 1·70 ± 0·12) (○), 1 083 (1·66 ± 0·13) (□), 1 113 (1·59 ± 0·08) (●), 1 163 (1·38 ± 0·10) (■), and 1 213 K (1·16 ± 0·11) (△)

The products of reaction were collected in the cooler region of the reaction loop. This was removed in a dry inert atmosphere and the products shown by chemical analysis [11] to be a mixture of WBr_5 and WBr_6. The WBr_6 was produced by reaction of Br_2 with WBr_5 in the cooler regions of the reaction loop.

Bromine and Nitrogen Mixtures.—The same range of bromine concentrations, *i.e.* 0·5—1·5 mol m^{-3}, was used, the total pressure of bromine + nitrogen being 100 Torr. Thus the $N_2 : Br_2$ ratio varied from 9 : 1 to 3 : 1. It was more difficult to obtain reproducibility with nitrogen present but the runs showed the same dependence on bromine pressure as before. However the rate was higher than predicted by simple dilution of the bromine. This effect was probably caused by small amounts of oxygen being introduced in the system with the nitrogen, as the characteristic orange colouration due to WBr_2O_2 was observed. The results are shown in Table 2.

TABLE 2

Rate of reaction for various ratios of bromine to filler gas

Run	Filler gas	T/K	p_{Br_2}/ mol m^{-3}	Total pressure (P/Torr)	10^{-14} Rate/ mol m^{-2} s^{-1}	
						*
(1)	N_2	1 163	1 467	98	11·5	7·4
(2)	N_2	1 163	1·174	100	6·2	4·8
(3)	N_2	1 163	1·174	100	6·1	4·8
(4)	N_2	1 163	0·880	100	4·4	2·5
(5)	N_2	1 163	0·587	100	1·5	1·05
(6)	N_2	1 163	0·880	100	3·8	2·5
(7)	Ar	1 163	1·467	100	8·0	7·2
(8)	Ar	1 163	1·467	100	9·3	7·2
(9)	Ar	1 163	1·467	100	16·2	7·2

* Predicted for simple dilution effect.

Bromine and Argon Mixtures.—Experiments were made using only one bromine concentration as it was found to be extremely difficult to obtain an oxygen-free mixture. The results in Table 2 show that the effect of argon was essentially the same as nitrogen, *i.e.* a simple dilution effect. Run (9) has been included to show the effect of trace amounts of O_2 impurity on the rate. The presence of oxygen leads to WBr_2O_2 (orange). The sequence of reactions being as in (1). This reaction has been studied in detail [2] and run (9) underlines the increase in reaction rate which results from traces of oxygen in the bromine.

DISCUSSION

The experimental data show that the reaction between tungsten and bromine is capable of a variable order, with the order with respect to bromine concentration changing from 1·70 to 1·16 over 150 K. It is probable that the initial product of reaction at the tungsten surface is one, or a combination, of WBr_2, WBr_3, WBr_4,

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[11] J. Tillack, *Z. analyt. Chem.*, 1968, **239**, 81.

or WBr_5, with the higher molar ratio of bromine predominating at the lower temperature. Tungsten pentabromide is known to have a gas-phase existence up to 1 800 K [12] and could therefore contribute to the higher orders. Tungsten dibromide has been shown to have a short gas-phase existence at temperatures around 1 100 K [12] and therefore could contribute. Above 1 100 K it has been shown to decompose to the elements [equation (3)] with the elements combining to form the

$$WBr_2(g) \longrightarrow W(s) + Br_2(g) \longrightarrow WBr_5(g) \quad (3)$$

pentabromide. The gas-phase existence of WBr_3 and WBr_4 is open to doubt; WBr_4 has been shown to undergo solid-state decomposition at temperatures in excess of 550 K [12] according to equation (4) and polymeric WBr_3

$$3WBr_4(s) \longrightarrow 2WBr_5(g) + WBr_2(s) \quad (4)$$

also undergoes dissociation at 590 K [13] to give WBr_2 and Br_2. The evidence suggests that the major species involved in the reaction at the surface are WBr_5 and WBr_2, but it is not certain whether the rate of dissociation of any WBr_3 or WBr_4 formed at the surface is too fast for them to act as transient rate-determining species in the overall reaction.

We now consider whether the bromine attack is molecular or atomic. The low value of the activation energy indicates that homogeneous dissociation of Br_2 cannot be involved in the rate-determining step since this would require a minimum energy of 197·2 kJ mol^{-1} at 1 173 K.[14] Heterogeneous dissociation at the surface cannot be ruled out, but, as bromine molecules are dissociated thermally to a considerable extent at the temperatures used, between 30 and 70% at 1 173 K [14] depending on the pressure, any such dissociation may be assumed to make only a small contribution. Probably, the major contribution to the activation energy is from adsorption of atomic bromine onto, and desorption of the products from, the tungsten surface. A study of the reactivity of atomic and molecular chlorine with molybdenum [5] has shown that the former reacts two orders faster than the latter. Assuming similar behaviour for bromine, then the high percentage of atomic bromine present leads to the conclusion that all reactions between bromine and tungsten involve atomic bromine at these temperatures.

At the lowest temperatures used the important surface-produced species could be WBr_n ($n = 2$—5), but the most likely is a combination of $n = 2$ and 5, and at the highest temperature the surface product is probably WBr_2 with a small contribution from WBr_5. The sequence of reactions can be represented as in (5)—(13). The concentration of product on the surface will be low and is unlikely to have any effect on the reaction rate. Tungsten pentabromide would volatilise immediately (b.p. 665 K [14]) and WBr_2 would react with either Br or Br_2 to form WBr_5 [13] and so be removed. The transportation of WBr_5 from the proximity of the tungsten surface would be swift as a result of the thermal-pump effect. The build-up of the tungsten bromide species on the surface is almost certainly by a stepwise process and the move from higher to lower reaction orders over the temperature range tends to indicate that each addition of atomic bromine is equally fast and therefore no individual step is rate determining. The reduction in order indicates that the predominant species moves from the more stable gas-phase species WBr_5 to the less stable WBr_2. This transition must be associated with some steric factor or increased desorption of bromine atoms from the surface with increased temperature.

$$Br(g) \longrightarrow Br(surf) \quad (5)$$

$$W(s) + Br(surf) \longrightarrow WBr(surf) \quad (6)$$

$$WBr(surf) + Br(surf) \longrightarrow WBr_2(surf) \quad (7)$$

$$WBr_2(surf) + Br(surf) \longrightarrow WBr_3(surf) \quad (8)$$

$$WBr_3(surf) + Br(surf) \longrightarrow WBr_4(surf) \quad (9)$$

$$WBr_4(surf) + Br(surf) \longrightarrow WBr_5(surf) \quad (10)$$

$$WBr_2(surf) \longrightarrow WBr_2(g) \quad (11)$$

$$WBr_5(surf) \longrightarrow WBr_5(g) \quad (12)$$

$$WBr_2(g) + 3Br(g) \longrightarrow WBr_5(g) \quad (13)$$

Fluorine attack of tungsten has been studied extensively,[4] the major product at low temperatures (800 K) being WF_6 whereas the major product at 2 000 K was WF. It was postulated that the reduction in fluorine content of the product resulted from increased desorption of adsorbed fluorine atoms from the surface and the variation in sticking factor with coverage and temperature. The W–Br bond is much weaker than the W–F bond and therefore appreciable desorption would be expected at lower temperatures. Unfortunately insufficient data are available to predict the precise temperature at which desorption becomes important, but published work [15] suggests that desorption of atomic bromine increases rapidly over the 1 063—1 213 K temperature range.

The experiments in which nitrogen and argon were used as ballast gas showed the expected reduction in rate, but they were not as would be expected for a straight dilution factor. As nitrogen is strongly chemisorbed on tungsten [16] in the temperature range employed and has a binding energy greater than that of bromine,[15] it would be expected that nitrogen would compete favourably for active sites resulting in a rate lower than that attributed to simple dilution. As all our reaction rates were in excess of that due to dilution, oxygen must have been participating. Chemisorbed oxygen on tungsten is known to prevent chemisorption of molecular nitrogen [17,18] and there is also evidence that oxygen can

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[12] V. W. Goddard, Ph.D. Thesis, Leicester University, 1971.

[13] R. Siepmann and H. Schafer, *Naturwiss.*, 1965, **52**, 344.

[14] JANAF Thermodynamical Tables, 2nd edn., NBS 37 1141P, June 1971.

[15] B. McCarroll, ' Structure and Chemistry of Solid Surfaces,' ed. G. A. Somorjai, Wiley, 1969, paper 61.

[16] G. Ehrlich, *J. Phys. Chem.*, 1956, **60**, 1388.

[17] B. McCarroll, *J. Chem. Phys.*, 1967, **46**, 863.

[18] D. E. Rosner and H. D. Allendorf, *J. Electrochem. Soc.*, 1967, **114**, 305.

displace chemisorbed nitrogen on tungsten.[18,19] Insufficient data are available for argon but the same general argument is probably true. Zubler [3] has shown that the surface reaction in the tungsten–oxygen–bromine system is dependent on ballast gas. In the higher-bromine-pressure region he found that the reaction rate decreased in the order nitrogen $>$ helium $>$ argon.

The electron micrographs showed that selective attack had taken place on the tungsten surface with the initial attack occurring at specific crystallographic planes. This was followed by a more general attack which produced a smoother surface containing local active sites.

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[19] J. H. Singleton, *J. Chem. Phys.*, 1966, **45**, 2819; 1967, **47**, 73.