trations of 10% gave results significantly poorer than the optimum.

(4) **Flow Rate.**—Figure 4 shows that the adsorption process is by no means instantaneous, and that therefore a slow flow rate is desirable for optimum column utilization. For columns packed with 28–200 mesh silica gel it was found that flow rates of 20 cm./hour based on the empty column were satisfactory; slower flow rates did not produce appreciable improvement in results.

It remains to investigate the possibility of concentration of hafnium by differential stripping of the silica gel. If a column is operated until the last effluent increment has a weight Hf/Zr ratio of 0.003, the last product being flushed out with methanol and the column drained, the silica gel will contain approximately 0.1 g. total oxide equivalent per gram silica gel, of which approximately 10% is hafnium oxide. Prolonged flushing with methanol (until effluent gives no further qualitative test) removes approximately one-half of the zirconium but very little hafnium, so that there remains on the gel 0.05 g. total oxide equivalent per gram silica gel, of which 20% is hafnium oxide. Further concentration can be obtained by stripping with 2.5 *M* anhydrous HCl in methanol; it is advantageous to use this solvent from the start of the stripping operation since less time and material are required to achieve the concentration from 10 to 20% than with pure methanol. The differential stripping is illustrated by Fig. 5. Nearly 90% of the adsorbed hafnium can be recovered as a 20% hafnium oxide–80% zirconium oxide product, 60% as a 30% hafnium oxide product, or about 20% as a 60% hafnium oxide product. It is not believed that further differential stripping is worthwhile because of rapidly decreasing yields. A concentrate in the 30–60% hafnium oxide range should be a highly satisfactory starting material for a liquid–liquid extraction concentration, however.

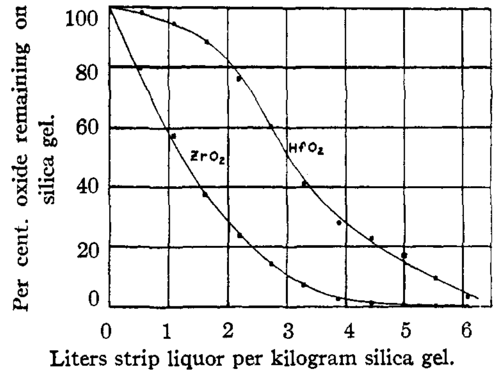

Fig. 5.—Differential stripping of Zr and Hf from silica gel with 2.5 molar HCl in methanol—120 lb. gel.

Final stripping is best achieved by use of an aqueous 7 *N* H_2SO_4 solution. Such stripping requires less than half the volume required for 2.5 *M* HCl in methanol, but is not differential. The silica gel can be reactivated and used again.

Acknowledgment.—Spectrographic analyses were performed by the spectrographic laboratory of the Ames Laboratory, A. E. C. under the supervision of and according to a method developed by V. A. Fassel and C. H. Anderson. The assistance of these workers is gratefully acknowledged. This work was performed in the Ames Laboratory, Atomic Energy Commission.

Summary

An adsorption purification of zirconium from hafnium has been discovered. Most satisfactory results have been obtained from the preferential adsorption of hafnium from a methanol solution of zirconium and hafnium tetrachlorides by silica gel. Other solvents have been investigated, as well as effects of concentration, flow rate and gel properties. Concentration of adsorbed hafnium to 30–60% products in good yields has been achieved by differential stripping.

AMES, IOWA RECEIVED MAY 11, 1950

[CONTRIBUTION FROM BALLISTIC RESEARCH LABORATORIES, ABERDEEN PROVING GROUND, MD.]

Chemiluminescence of the Sodium or Sodium Halide Catalyzed Oxidation of Carbon Monoxide by Nitrous Oxide[1]

BY CHARLES P. FENIMORE AND JOHN R. KELSO

While Bawn[2] showed that the oxidation of carbon monoxide by nitrous oxide involves both heterogeneous processes and gas phase chain reactions, he did not study the effect of varying the nature of the surface. There are marked differences between the reactions in sodium halide coated and in clean vessels; although the most interesting differences appear to be due not to a variation in the heterogenous reaction, but to a small amount of sodium vapor in the gas phase (formed from the sodium halide), and to the reluctance of nitrous oxide to transfer its oxygen atom directly to carbon monoxide. We suggest that free sodium atoms catalyze the oxidation of carbon monoxide with simultaneous emission of the sodium resonance lines. We formulate the catalysis

$$\mathrm{Na} + \mathrm{N_2O} \longrightarrow \mathrm{NaO} + \mathrm{N_2}$$
$$\mathrm{NaO} + \mathrm{CO} \longrightarrow \mathrm{CO_2} + \mathrm{Na}^*(^2\mathrm{P})$$
$$\mathrm{Na}^* \longrightarrow \mathrm{Na} + h\nu$$

---

[1] Presented at the American Chemical Society meeting in Detroit, Mich., April, 1950.

[2] Bawn, *Trans. Far. Soc.*, **31**, 461 (1936).

and confirm this by studying the addition of sodium vapor to a mixture of nitrous oxide and carbon monoxide at a temperature too low for an uncatalyzed reaction to occur. Our work, however, does not elucidate the mechanism of formation of sodium atoms from the sodium halide.

Experimental

The sodium halide catalyzed reaction was studied in quartz vessels, 2.5 cm. inside diameter, 30 cm. long. These were placed horizontally in a cylindrical resistance furnace. The temperature, which varied over the length of the reaction vessels because the end of the furnace away from the gas inlet was left open to observe the emitted light, decreased only about 5° along the first 25 cm. from the inlet, but fell drastically in the last 5 cm. The temperatures recorded in the figures or stated in the paper are those measured half way down the vessel.

The light emitted during the slow reaction was observed visually, photographically, or spectroscopically end-on through the open furnace. A small quartz prism spectrometer (incapable of resolving the sodium D lines) was used for the spectroscopic observations with Eastman type F film. No light other than yellow sodium or red lithium light (from lithium chloride coated vessels) was ever photographed during the slow reaction.

Nitrous oxide and carbon monoxide were drawn from gas cylinders and freed from oxygen, carbon dioxide, iron carbonyl and water. It was established that the addition of 2% hydrogen to the reaction mixtures had only a small effect on the rate of carbon dioxide formation or on light intensity. Nitric oxide was prepared by the reduction of nitrite ion, oxygen was obtained from gas cylinders.

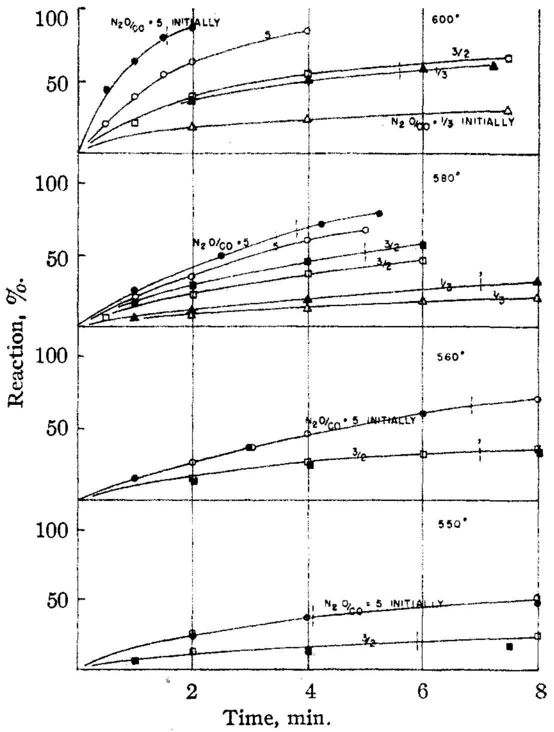

Fig. 1.—Reaction of nitrous oxide, carbon monoxide mixtures in clean quartz (open symbols) and in sodium chloride coated quartz vessels (filled symbols), total pressure = 85 mm. Initial ratio (N_2O/CO) is indicated on each curve. Dotted lines (⁝) indicate times at which the light emission from the sodium chloride coated vessel becomes inappreciable.

The gas in the reaction vessel could be drawn into a previously evacuated vessel at any time for analysis. This was run in a Blacet, MacDonald and Leighton microanalysis apparatus over mercury, using as absorbents: potassium hydroxide for carbon dioxide, phosphorus for oxygen, and determining carbon monoxide and nitrous oxide by combustion with an excess of the other or with added oxygen. Neither nitric oxide nor nitrogen dioxide was formed in the slow reaction; 1–2% of oxygen was found in the mixtures rich in nitrous oxide after 60–80% of the oxidation reaction had occurred, however; and when 4% of nitric oxide was added to certain mixtures, a little color due to nitrogen dioxide was observed in the samples drawn off. In most of the analyses only carbon dioxide was determined.

In clean quartz, our reaction rates were considerably less than those observed by Bawn although they showed a similar dependence on gas composition and corresponded to his findings at temperatures about 30° lower than ours. Probably this difference can be ascribed to our non-uniform temperatures. A further difference is the following: Bawn found that although the explosive reaction was markedly inhibited by nitric oxide in his clean isothermal vessels, the slow reaction was not; and our contradictory observation (Fig. 2) indicates that temperature inequalities through the vessel permitted us to obtain a characteristic in the slow reaction which in an apparatus at uniform temperature can be observed only in the explosive reaction.

The sodium induced oxidation of carbon monoxide by nitrous oxide was studied in an apparatus such as is used in the "diffusion method" for atomic reactions. A measured volume of a carrier gas (nitrogen or nitrogen mixed with carbon monoxide) at 3–9 mm. pressure flowed over sodium metal at 300° and through a 3 mm. diameter orifice into a heated, larger, concentric reaction tube to which nitrous oxide was separately admitted at a known rate and at a lower partial pressure. When the desired steady state had been attained, the gases leaving the reaction tube were passed through traps cooled with liquid nitrogen and eventually to the pumps. The gas frozen out could be vaporized at the end of the experiment, measured, and analyzed for the carbon dioxide and nitrous oxide. No other gas was condensed. Assuming the carrier gas saturated with sodium vapor, one can calculate the number of molecules of carbon dioxide formed per sodium atom burned, while if this assumption is incorrect, the calculated yield of carbon dioxide per sodium atom is still a lower limit. The strikingly increased emission of the D lines accompanying the catalysis could be observed visually or photographically on changing the carrier gas from nitrogen to a mixture of nitrogen and carbon monoxide.

The Sodium Halide Catalyzed Reaction.—In Fig. 1, rate curves are presented for the slow reaction in clean and in sodium chloride coated quartz vessels. The effect of coating the vessel is to leave the rate almost unchanged at 560° and at lower temperatures, but to increase the temperature dependence of the reaction moderately above 560°. The increased reaction velocity in the salted vessel is shown in the greater ease of explosion as well; for at 600°, a mixture of nitrous oxide/carbon monoxide = 3/2 exploded at 85 mm. pressure after a 5-sec. induction period; and the slow reaction of other compositions at 85 mm. could not be studied at 620° in the salted vessel because of explosions. In the clean vessel, however, the slow reaction persisted up to at least 640°.

It is remarkable that in the sodium chloride or bromide coated vessel, the slow reaction proceeds with the emulsion of yellow sodium light, λ =

5890 Å. When the vessel is viewed end-on, the light appears to fill it uniformly except very near the wall where the intensity is small. From photographs of the glowing reaction vessel, the intensity was found to vary slightly across the diameter, even away from the wall, and to be greatest at the center. It fades slowly with time but persists for as long as 6–8 min., or until the rapid change of composition with time has slowed. In Fig. 1, dotted vertical lines are drawn at the times when the light intensities become very weak. If an identical vessel is coated with lithium chloride, the slow reaction starts with the emission of red lithium light, λ = 6708 Å., which varies with changing circumstances much as does the sodium light except that it persists for only a few seconds. In a vessel with potassium chloride or sodium iodide coating or in clean quartz, no light emission accompanies the slow reaction. The potassium chloride coated vessel was investigated over a 40° range with the three gas compositions indicated in Fig. 1, but the sodium iodide coated vessel only with nitrous oxide/carbon monoxide = 3/2 at 580° because this salt released a large amount of iodine when the gas mixture was admitted. The liberated iodine obviously poisoned the luminescence because a vessel coated with mixed sodium chloride and iodide did not emit the sodium lines.

The light intensity is comparatively feeble at 550 and 560° and greatly increases toward higher temperatures. At a fixed temperature it is strongest when the reaction is fastest and both light intensity and reaction rate can be greatly decreased together (by the addition of nitric oxide) or increased together (by the addition of molecular oxygen), Fig. 2. We conclude that reacting mixtures of nitrous oxide and carbon monoxide excite the sodium and (less successfully) the lithium lines, but only when the gases are reacting.

Attempts to excite sodium light by the slow reaction of carbon monoxide and oxygen in the sodium chloride coated vessel failed. The attempt was carried out above the upper explosion limit by loading the vessel at 580° with a stochiometric mixture to 200 mm. and raising the temperature until a fairly rapid reaction took place, at about 650°. The gases were sampled and the rate was found to be comparable to the rates observed with nitrous oxide and carbon monoxide at about 560° (50% of complete reaction within eight minutes).

The observed sodium light requires free metal atoms in the system but the question of their origin cannot be satisfactorily answered. If their formation occurs through the non-equilibrium absorption of energy by the sodium halide from a process occurring in the reaction, the effect of the additives (Fig. 2) is consistent with

$$CO + O \longrightarrow CO_2 + 126.7 \text{ kcal.}$$

as a possible source of the dissociation energy. It is uncertain, however, whether the free sodium atoms are formed at the wall or in the gas phase (the vapor pressure[3] of these halides is of the order of 0.001–0.01 mm. at the temperatures of the experiments).

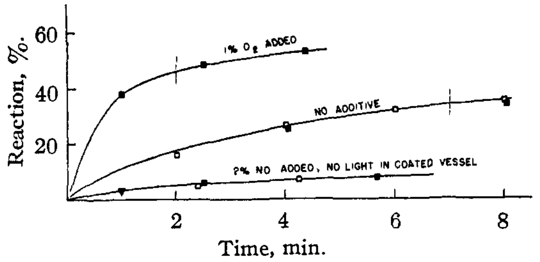

Fig. 2.—Effect of added oxygen and nitric oxide on the nitrous oxide, carbon monoxide reaction at 560°, pressure = 85 mm.; initial composition, (N_2O/CO) = 3/2. Filled symbols refer to sodium chloride coated vessel, open symbols to clean quartz. Dotted lines have the same significance as in Fig. 1. Light intensity far greater for upper than for middle curve.

Whatever the manner of formation of sodium atoms from the sodium halide, the observed catalysis and simultaneous light emission can be assigned a mechanism which will be shown to be rather probable. Bawn and Evans[4] have proposed from a study of the reaction between sodium vapor and nitrous oxide that the process

$$\text{(a)}\quad Na + N_2O \longrightarrow N_2 + NaO + 30.5 \text{ kcal.}$$

occurs once in every forty collisions at 300°. The reactions

$$\text{(b)}\quad NaO + CO \longrightarrow CO_2 + Na^*(^2P) + 7.5 \text{ kcal.}$$

$$\text{(c)}\quad Na^* \longrightarrow Na + h\nu$$

are energetically possible and, if they occurred, could account simultaneously for the increased reaction rate and for the considerable light emission.

The Sodium Induced Oxidation of Carbon Monoxide by Nitrous Oxide.—Using the same type of apparatus as Bawn and Evans, we have shown that the catalytic cycle postulated above occurs indeed. Nitrogen or nitrogen plus carbon monoxide, saturated with sodium vapor at 300°, was streamed into nitrous oxide in a reaction chamber at 350–375°. The velocity of the carrier gas was generally about 1.7×10^{-5} mole/sec., and the duration of a run, 1–1.5 hours. Nitrous oxide and carbon dioxide were determined in the gaseous reaction products which were condensable by liquid nitrogen, and the carbon dioxide formed per atom of sodium admitted to the reaction vessel was then calculated. The results obtained are listed in Table I.

The first three runs demonstrate that all three reactants (sodium, carbon monoxide and nitrous

---

[3] Vapor pressure estimates in this paper are taken from Kelley, "The Free Energies of Vaporization and Vapor Pressures of Inorganic Substances," Bureau of Mines Bulletin 383, U. S. Dept. of the Interior, 1935.

[4] Bawn and Evans, *Trans. Faraday Soc.*, **33**, 1571 (1937).

TABLE I

SODIUM INDUCED OXIDATION OF CARBON MONOXIDE BY NITROUS OXIDE

		Reactants,[a] mm.			Analysis of condensate, %		Yield,	Yield/
Run	T	P_{N_2}	P_{CO}	P_{N_2O}	CO_2	N_2O	CO_2/Na	P_{N_2O}
1	375	4.40	2.20	0.88	0	98	Na omitted	..
2	350	7.80	0	0.77	0	96	0	..
3	350	6.00	3.00	0	no condensate		0	..
4	350	5.16	2.57	0.77	43	57	24	31
5	350	4.17	1.33	0.83	40	60	24	29
6	350	2.54	1.27	0.19	33	65	4.5	24
7	375	4.29	2.14	1.07	42	59	32	30

[a] N_2 and CO were saturated with Na at 300° (P_{Na} = 0.014 mm.) in all runs except the first.

oxide) must be present to obtain carbon dioxide and the increased light emission. The increase in emitted sodium light when the nitrogen carrier gas is replaced by a mixture of nitrogen and carbon monoxide is illustrated in Fig. 3, which reproduces otherwise identical photographs of the reaction vessel taken during runs 2 and 4.

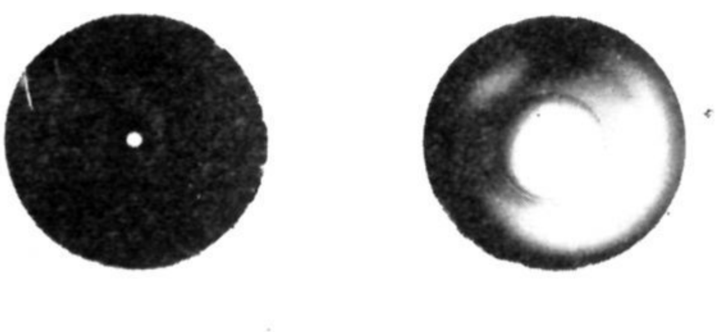

Fig. 3.—End-on photographs of the reaction vessel showing sodium vapor burning in nitrous oxide in absence of carbon monoxide (run 2, to left) and in presence of carbon monoxide (run 4, to right). The photographic conditions were identical.

A comparison of runs 4 and 5 shows that the yield of carbon dioxide is independent of the partial pressure of carbon monoxide; and of runs 5 and 6, that the yield of carbon dioxide per sodium atom varies approximately directly with the partial pressure of nitrous oxide. If one ignores the ultimate loss of sodium from the reaction cycle and applies a steady state treatment of the suggested equations, then

$$d(CO_2)/dt = k_a(Na)(N_2O)$$

and the observed results are approximately those expected. Run 7 demonstrates that the temperature dependence of the catalytic reaction is small when sodium metal is present as one of the reactants. In the salt coated vessel, of course, the catalytic reaction possesses a rather large temperature dependence because of the necessity of forming gaseous sodium atoms.

If nitrous oxide is replaced by oxygen, no light emission occurs; nor are the potassium lines observed if sodium at 300° is replaced by potassium at 220° (P_K = 0.016 mm.)—the latter observation is consistent with the failure of light emission from the potassium chloride treated vessel at 560–600°. If the carbon monoxide in the carrier gas is replaced by hydrogen, the effect of light emission is as if the carrier gas were pure nitrogen.

It can scarcely be doubted that the mechanism of the sodium induced oxidation at 350–375° is operative in the sodium halide vapor, nitrous oxide, carbon monoxide system at 550–600° as well. Evidence of identical mechanism is furnished by the observation that the ratio of carbon dioxide formed in the catalyzed reaction to sodium light emitted is approximately the same in the two systems; a result obtained by comparing a series of photographs of the reaction vessels (roughly of equal size) and noting that when the sodium chloride catalyzed reaction required eight times as long as the sodium catalyzed reaction to produce the same integrated film blackening, the rate of carbon dioxide formation in the latter system was ten times as great as the difference between the rates of carbon dioxide formation in the sodium chloride coated and the clean quartz vessel. The errors in the comparison are considerably greater than the difference between eight and ten, what is proven is only that the two numbers are of the same order of magnitude.

Acknowledgment.—We are grateful to Mr. Arthur Thrailkill for his valuable aid in the spectroscopic observations.

Summary

At 550–600° in reaction vessels coated with sodium chloride or bromide and possessing temperature inequalities, the slow reaction of carbon monoxide and nitrous oxide is catalyzed by the alkali halide with simultaneous emission of the sodium resonance lines. The catalytic and luminescent reactions postulated are

$$Na + N_2O \longrightarrow NaO + N_2$$
$$NaO + CO \longrightarrow CO_2 + Na^*(^2P)$$
$$Na^* \longrightarrow Na + h\nu$$

and these are confirmed through a subsidiary study of the sodium induced oxidation of carbon monoxide by nitrous oxide at 350–375° and a comparison of the light yield in the two reaction systems.

The mechanism of the formation of sodium atoms from sodium chloride or bromide is uncertain.

The slow nitrous oxide, carbon monoxide reaction does not excite the metal lines in potassium chloride or sodium iodide coated vessels (potassium vapor does not undergo the analogous chemiluminescent catalytic cycle, and iodine is a reaction poison). It does, however, briefly excite the red lithium line in a lithium chloride coated vessel.

ABERDEEN PROVING GROUND, MARYLAND

RECEIVED APRIL 17, 1950