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NOTE

On the Use of a Quadrupole Residual Gas Analyzer for a Continuous Scan of the Products in a Low-Pressure Catalytic Flow Reactor

The objective of this note is to communicate certain observations pertinent to the use of a Quadrupole Residual Gas Analyzer for catalytic studies at low pressures in a flow system.

In an attempt to study the surface properties of iron-chromium alloys (in the form of high-purity wires) the decomposition of nitrous oxide flowing at the rate of a few cubic millimeters per hour over the alloy wire maintained at a specific temperature has been measured. The system employed the Quadrupole Residual Gas Analyzer (Varian Associates) for a continuous scan of the products and for an analysis of any variation in product distribution with time; it was pumped by an oil diffusion pump (1000 liter/sec) and a mechanical pump. In order to eliminate any interference due to oil vapor contamination, a liquid nitrogen trap was inserted between the oil diffusion pump and the Quadrupole. A schematic diagram of the set up used is shown in Fig. 1.

With no decomposition (catalytic or thermal occurring in the sample cell, the cracking pattern obtained for N_2O in the Quadrupole revealed an oxygen peak (at mass 32) in the spectrum and could not be matched either with the API cracking pattern or that provided by Varian. The extent of the oxygen in the spectrum was approximately 10% of the peak at 44 (N_2O) in the pressure range 10^{-4} to 10^{-5} torr. A variety of experiments indicated that the oxygen in the spectrum was not due to any leak into the system. The purity of the N_2O (Chemically Pure, supplied by J. T. Baker and Co., Phillipsburg, New Jersey) in different parts of the flow system was checked independently in a mass spectrometer (Hitachi Perkin Elmer RMU-6E) and revealed no detectable oxygen. While experiments were normally made at an emission current of 1 mA ($\sim$ 120 eV), the appearance of oxygen in the spectrum was independent of the emission current in the range, 0.03 to 3 mA, investigated. A switch from a thoriated iridium filament in the Quadrupole to a rhenium filament showed no oxygen in the spectrum at the start, but a gradual increase developed in the first 2 hr. Subsequently, the oxygen level in the spectrum remained constant as observed for the next 8 hr of operation. Our observations certainly preclude the possibility of (i) a leak into the system, (ii) oxygen contamination in the N_2O, and (iii) desorption of any oxygen by electron bombardment from the cage walls of the Quadrupole. It seems the oxygen detected was being produced continuously by the decomposition of N_2O in the Quadrupole.

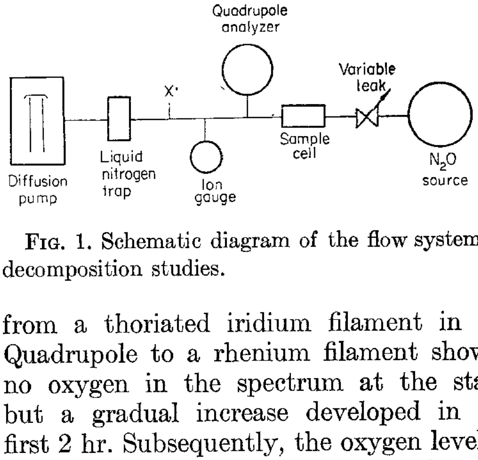

FIG. 1. Schematic diagram of the flow system for decomposition studies.

It was thought that the appearance of oxygen in the spectrum could be due to

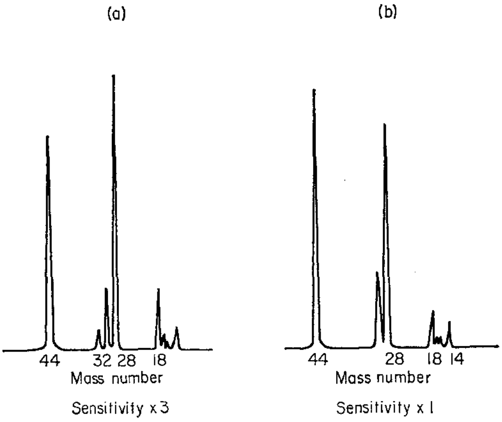

FIG. 2. Comparison of cracking pattern for N_2O (a) before and (b) after addition of VacIon pump to the system.

a conductance limitation and a consequent low pumping speed at the Quadrupole since some 8 ft of glass tubing, two right angle bends, and a liquid nitrogen trap separated the Quadrupole from the diffusion pump. The pump could not be brought any closer to the Quadrupole because of the continued necessity of a liquid nitrogen trap to protect it from oil contamination. Indeed the pumping speed, S_p, of the diffusion pump at the Quadrupole, calculated from the dimensions of the connecting tubes [for details see ref. (*1*)], showed it was approximately 0.6 liter/sec, while the maximum possible pumping speed of the Quadrupole filament, S_f, obtained from the equation

$$S_f = AC\alpha$$

where A is the surface area of the quadrupole filament, C, the conductance of N_2O at room temperature, and

$$\alpha = \frac{\text{rate of } N_2O \text{ decomposition}}{\text{rate of collision of } N_2O} \quad \text{(on the filament)}$$

was approximately 1.2 liter/sec.

To improve the conductance without the problem of contamination, an 8 liter/sec VacIon pump (Varian Associates) was added to the system (point X in Fig. 1) close to the outlet of the Quadrupole tube. A recalculation of the pumping speed, S_p, at the Quadrupole following the addition of the VacIon pump showed an increase from 0.6 to 4.5 liter/sec. The new value was clearly in excess of the pumping speed, S_f, attributed to the filament. A subsequent examination of the cracking pattern of N_2O showed no significant amount of oxygen. Figure 2 shows a comparison of the cracking pattern of N_2O (a) before and (b) after the addition of the VacIon pump to the system. If the VacIon pump was turned off when the diffusion pump remained on, oxygen reappeared in the cracking pattern. Figure 3 shows a variation of the peak height of oxygen with time at a constant flow of N_2O with and without the VacIon Pump. That the observed removal of oxygen is not due to any preferential pumping of oxygen by the ion pump was demonstrated by the appearance of oxygen (at mass 32) in the Quadrupole when a mixture of 99% N_2O and 1% of O_2 was used instead of pure N_2O.

These observations can be explained as being due to a decomposition of N_2O on the filament in the pressure range 10^{-4} to 10^{-5} torr followed by accumulation of oxygen on the filament prior to desorption. Thus

$$N_2O(g) \rightarrow N_2O(ads) \quad (1)$$

$$N_2O(ads) \rightarrow N_2(g) + O(ads) \quad (2)$$

and

$$O(ads) + O(ads) \rightarrow O_2(g) \quad (3)$$

In general for the system under consideration it can be easily shown that

$$\frac{P_{O_2}}{P_{N_2O}} = \frac{\text{“Effective” pumping speed of filament for } N_2O}{\text{“Available” pumping speed for oxygen}}$$

where P_{O_2} and P_{N_2O} refer to the partial pressures in the Quadrupole chamber. The ratio on the left-hand side can be minimized by providing suitably large pumping speeds. The addition of the VacIon pump to the system, which produces a threefold decrease in pressure (to 5×10^{-6} torr as determined from the integrated area under the peaks)

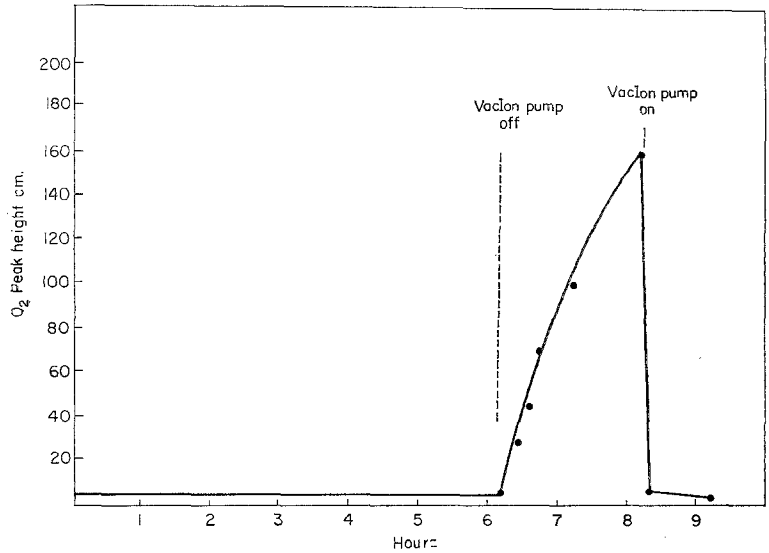

FIG. 3. Variation of peak height of oxygen (32) with time and pumping speed.

is thus seen suppressing interactions suggested in Eqs. (1) to (3).

Support for this conclusion also comes from an examination of the N_2/N_2O ratio in the Quadrupole chamber under different conditions of pumping. This ratio has a value of 1.29 in the system without the VacIon pump and decreases to ~ 0.80 on addition of the VacIon pump. Since N_2 is produced (a) in the cracking of N_2O due to electron bombardment and (b) in the decomposition on the filament, minimizing the decomposition on the filament could very well explain a decrease in the ratio. It is interesting to point out here that this ratio is further reduced to ~0.6 in the Varian cracking pattern obtained with the use of a nude guage where the effective pumping speed (S_p) close to the chamber was 20 liter/sec.

Thus, our experiments clearly show the importance of using large net pumping speeds with a Quadrupole Residual Gas Analyzer for product analysis in conventional flow systems.

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