Oscillations of the Platinum-catalysed Oxidation of Carbon Monoxide Induced by Inhibitors

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Summary Isothermal oscillations in the heterogeneous oxidation of carbon monoxide on platinum have been induced in an open system by the addition of low concentrations of organophosphorus compounds to the system.

IN the course of studies on the poisoning and inhibition of heterogeneous catalytic reactions, we have observed that sustained oscillations in the rate of oxidation of carbon monoxide over platinum can be induced by the addition of low concentrations of organophosphorus compounds to the system. Induced oscillations of this type in an open system seem not to have been described before and are of potential importance in the use of platinum catalysts in vehicle exhaust emission control, where organophosphorus compounds originating in the fuel or lubricating oils have already been reported to cause inhibition.[1]

A coil of platinum wire was mounted in the centre of a horizontal glass tube (15 mm i.d.) with its long axis at right angles to the gas flow. The coil (11 turns, 2 mm length, 0·75 mm diameter) was made from platinum wire (Goodfellow Metals), spot welded to a TO-5 transistor header. This coil formed one arm of a self-balancing bridge circuit. The temperature of the coil as measured by its resistance (*ca.* 1·4 Ω at 25 °C) was found to be constant to <2 °C even when oscillations were occurring. The concentrations of carbon monoxide and isopropyl methylphosphonofluoridate (Sarin) in the air flow (400 ml min^{-1}) down the tube containing the catalyst were 2·5% v/v and 4 μg l^{-1} respectively. Rates of oxidation were measured using the isothermal technique described previously.[2]

The pattern of oscillations was found to depend markedly upon the reaction temperature. It varied from trains of simple oscillations (Figure, a) at 385 °C to more complex functions at 425 °C (Figure, b). The reaction rate at both these temperatures is controlled by mass transport of carbon monoxide to the catalyst surface. When the inhibitor flow was turned off, oscillations (or more accurately switches or pulses of reduced oxidation) persisted at decreasing but irregular intervals for up to an hour or so.

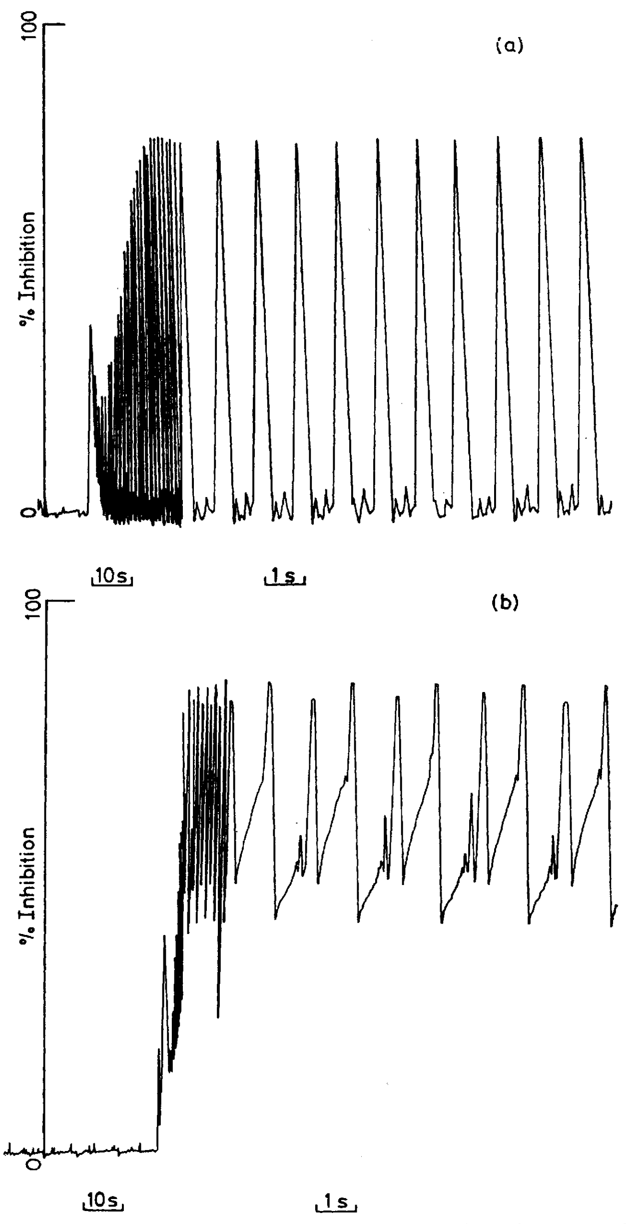

FIGURE. Inhibition of the Pt-catalysed oxidation of CO (2·5% v/v) in air by isopropyl methylphosphonofluoridate (4 μg l^{-1}): (a) at 385 °C; (b) at 425 °C.

Spontaneous oscillations of the Pt-catalysed oxidation of carbon monoxide have been reported by other workers[3] although insufficient control of the temperature of the catalysts was made to substantiate the claim that they were not thermokinetic in nature; a thermokinetic model for similar oxidations has been proposed.[4] Even if isothermal conditions can be assumed, the truly spontaneous nature of these oscillations is open to doubt since the intervention of traces of inhibitors which could induce oscillations cannot always be ruled out. For example, although it was possible to produce 'spontaneous' oscillations, at lower temperatures than those reported above, of carbon monoxide on Pt in the present system apparently with no inhibitor present (*i.e.* without the gas-flow line containing Sarin vapour), it was never possible to generate such oscillations when the air was filtered by active charcoal in a system in which no inhibitor had ever been used. As this oscillation-inducing behaviour is not unique to Sarin (triethyl phosphate behaves similarly) traces of inhibitor inducing the oscillations observed by other workers cannot be discounted.

Preliminary experiments with other oxidisable materials have indicated that the carbon monoxide–Pt system is not unique in oscillating in the presence of Sarin. We have ourselves observed similar behaviour during the platinum-catalysed oxidations of octane, hexane, and propan-1-ol in the presence of Sarin but not during oxidation of hydrogen.

We thank Professor P. Gray and Dr. J. Griffith, University of Leeds, for discussions.

(*Received*, 1*st July* 1977; *Com.* 662.)

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