

## LETTERS TO THE EDITOR

## ACTIVE SITES ON GOLD CATALYST: A MODEL

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ACCORDING to Bhakta and Taylor<sup>1</sup>, gold catalyst when heated at higher annealing temperatures ( $T_Q$ ) for a specified time, followed by quenching at liquid air temperature, acquired enhanced activity towards dehydrogenation of formic acid vapour (a probe reaction) at a lower annealing temperature ( $T_A$ ); the excess activity underwent decay according to no definite rate law. The present attempt, therefore, is to reanalyse their data and see if the kinetics of the decay of the enhanced activity parallels those of the other recovery processes in metals; because such a parallelism would be a clear pointer to the existence of a possible nexus between the catalytic and the other physical properties of metals.

In the present analysis,  $T_A$  is 403° K and  $T_Q$  is either (A) in the range 488°–678° K or (B) > 678° K.

(A) The enhancement of the activity upon quenching from  $T_Q$  and its subsequent decay at  $T_A$  is reversible. Assuming that the decay is a function of time only

$$a_t = a_1 t^{-n} \quad (1)$$

$a_1$  and  $a_t$ , expressed in number of molecules of formic acid monomer decomposed  $\text{cm}^{-2} \text{sec}^{-1}$  are the activity of the catalyst after 1 hour and  $t$  hour of annealing respectively; generally,  $t$  is in the range 0.5–10.0 hr, when about 35% of the enhanced activity would have decayed; as  $t$  increases,  $a_t \rightarrow a_A$ , the normal activity of the catalyst at  $T_A$ ;  $n$  is a constant, to be determined from experimental data.

As the induction of  $a_1$  is an activated process

$$a_1 = A \exp(-E'/RT_Q) \quad (2)$$

$A$ , a constant;  $E'$ , the apparent energy of activation of the enhancement process, 3940 cal/mole<sup>1</sup>.

Thus,

$$a_t = A [t \exp(-E/RT_Q)]^{-n} \quad (3)$$

where

$$E = E'/n$$

$$\text{or, } \log a_t + E/2.303 RT_Q = -n \log t + \log A \quad (4)$$

$(\log a_t + 3940/4.6 T_Q)$  values are plotted against  $\log t$  in Fig. 1, which incorporates 46 readings obtained from 13 experiments in which the decay rate was moderate; two different catalyst samples were used.

This analysis, based on equation (3), clearly indicates that the decay of the enhanced catalytic activity

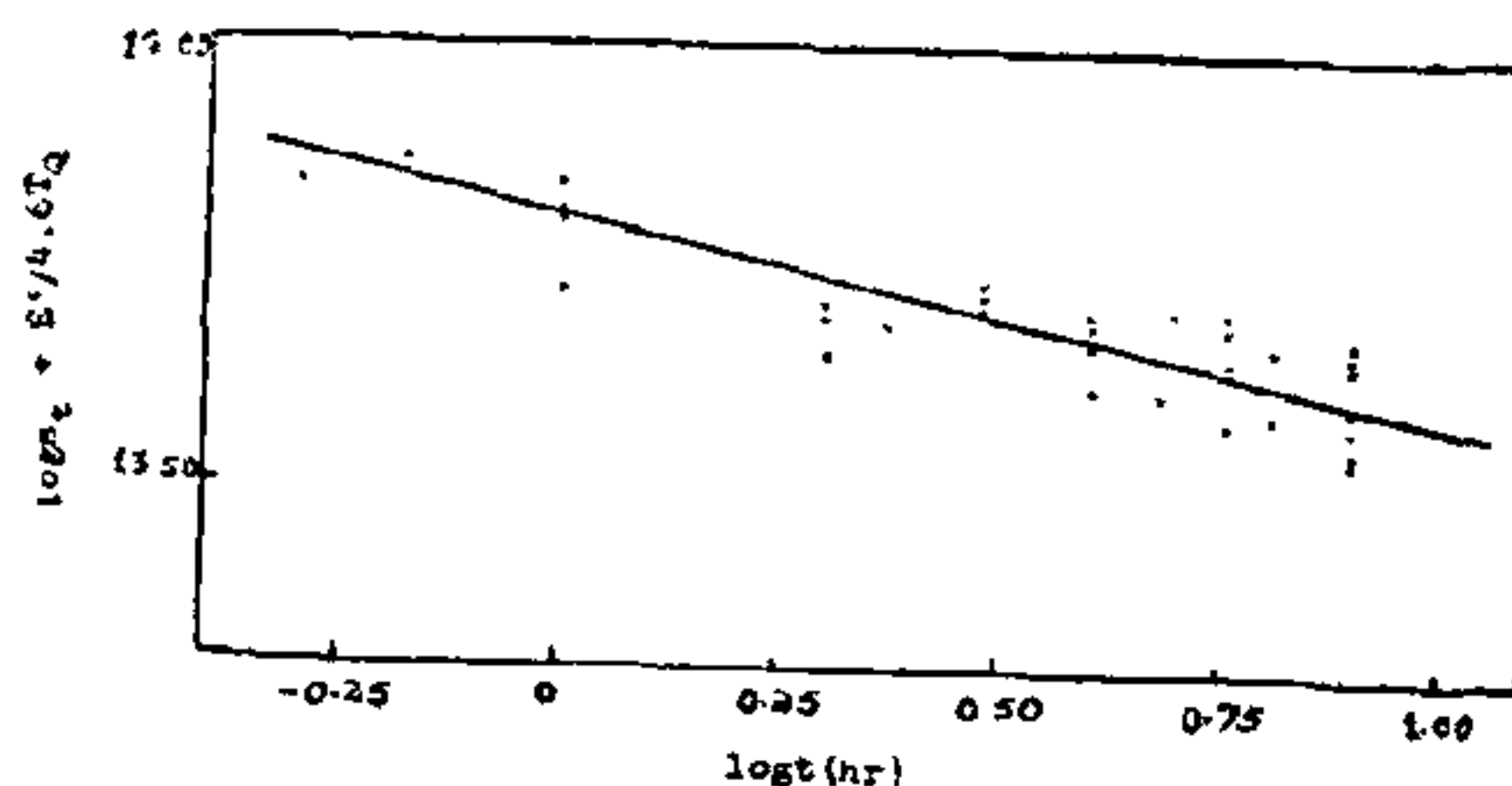


FIG. 1

$\log A = 13.80 \pm 0.04$ ; this agrees well with 13.72<sup>1</sup> (when the reaction volume is 9l ml).

$n = 0.21$ ; however,  $n$  appears to vary from 0.10 for the slow decay processes to 0.40 or 0.60 for the fast ones.

$E = 3940/0.21 = 18.75$  kcal/mole; the proximity of this value to 0.82 eV, the energy of migration for mono-vacancies is noteworthy.

is a "temperature-compensated time" a process typical of such processes as transient creep, recrystallisation, recovery of electrical resistivity, etc.<sup>2</sup>

(B) At  $T_Q > 678^\circ \text{K}$  the activities of both the catalyst samples dropped to a negligible value, apparently, irreversibly. This observation was not reported earlier<sup>1</sup> as it was considered irrelevant to the discussion in hand, then; however, now in the light of reports of similar drops in the activities of cold-worked metal catalysts<sup>3-6</sup> it assumes special relevance.

In the light of this analysis it is possible to offer the following tentative model for the catalytically active sites:

1. The surface terminations of dislocations, first suggested by Cratty and Granato<sup>7</sup> are the most favoured sites. Each termination point may be likened to a conical pit (etch pit) containing many steps of atomic dimension so that each pit can be regarded as an ensemble of 'micro' sites (steps).  $n_d$ , the density of dislocation pits remains largely unchanged at  $T_Q < 678^\circ \text{K}$ . At  $T_A$ , for instance, if  $\bar{n}_{s(A)}$  be the average number of steps per pit, then there are  $n_d \bar{n}_{s(A)}$  sites  $\text{cm}^{-2}$ .

2. Heating the catalyst at  $T_Q < 678^\circ \text{K}$ , generates vacancies whose diffusion to the surface (preferably, via dislocations) tend to widen and deepen the pits and proliferate the steps therein. If  $\bar{n}_{s(Q)}$  be the average number of sites per pit at  $T_Q$  then, there are at  $T_Q$ ,  $n_d \bar{n}_{s(Q)}$  sites  $\text{cm}^{-2}$ ; obviously,  $n_d \bar{n}_{s(Q)} > n_d \bar{n}_{s(A)}$ .

3. Upon quenching from  $T_Q$  the situation obtaining at  $T_Q$  is 'frozen'; therefore, at the lower temperature  $T_A$ , the catalyst retains a large fraction of  $n_d \bar{n}_s(Q)$  and, consequently, exhibits an activity larger than its true value at  $T_A$  (proportional to  $n_d \bar{n}_s(A)$ ).

4. Eventually, at  $T_A$  all the excess vacancies diffuse out *via* dislocations and the pits are restored to their original dimensions and the catalyst, to its original activity ( $a_i \rightarrow a_A$ ). The decay process, may, therefore, be likened to the 'healing of a scratch' or other time-dependent recovery processes.

5. At  $T_Q > 678^\circ \text{K}$  there is a drastic and, perhaps, irreversible reduction in  $n_d$  and, therefore, of the catalytic activity.

This model, on the one hand, is able to explain adequately, though qualitatively, the activity of cold-worked metal catalysts and the effect thereon of annealing at various temperatures, while on the other, it can account for the failure of Bagg *et al.*<sup>8</sup> to experimentally detect one to one correspondence between  $n_d$  (instead of  $n_d \bar{n}_s$ ) and the catalytic activity.

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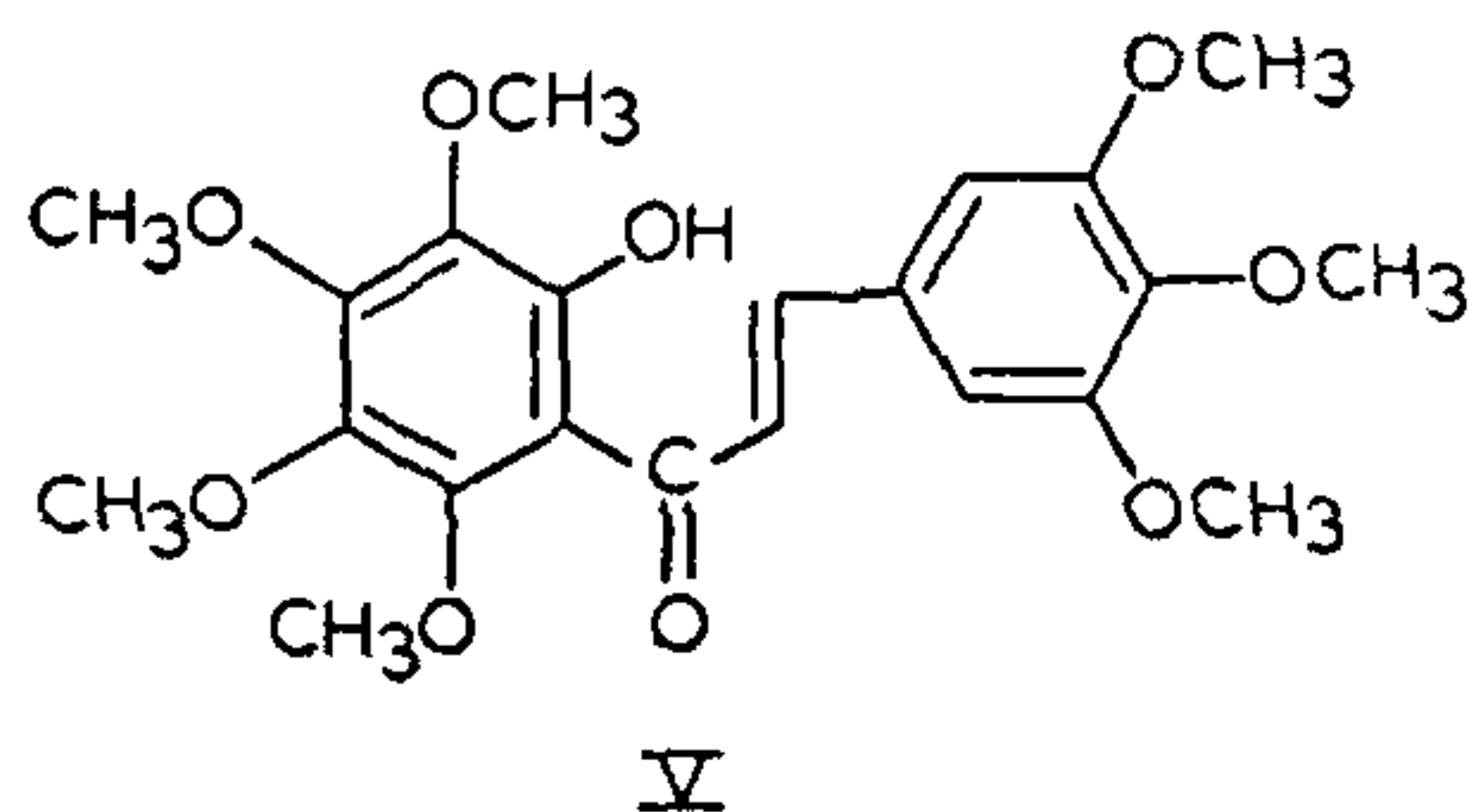
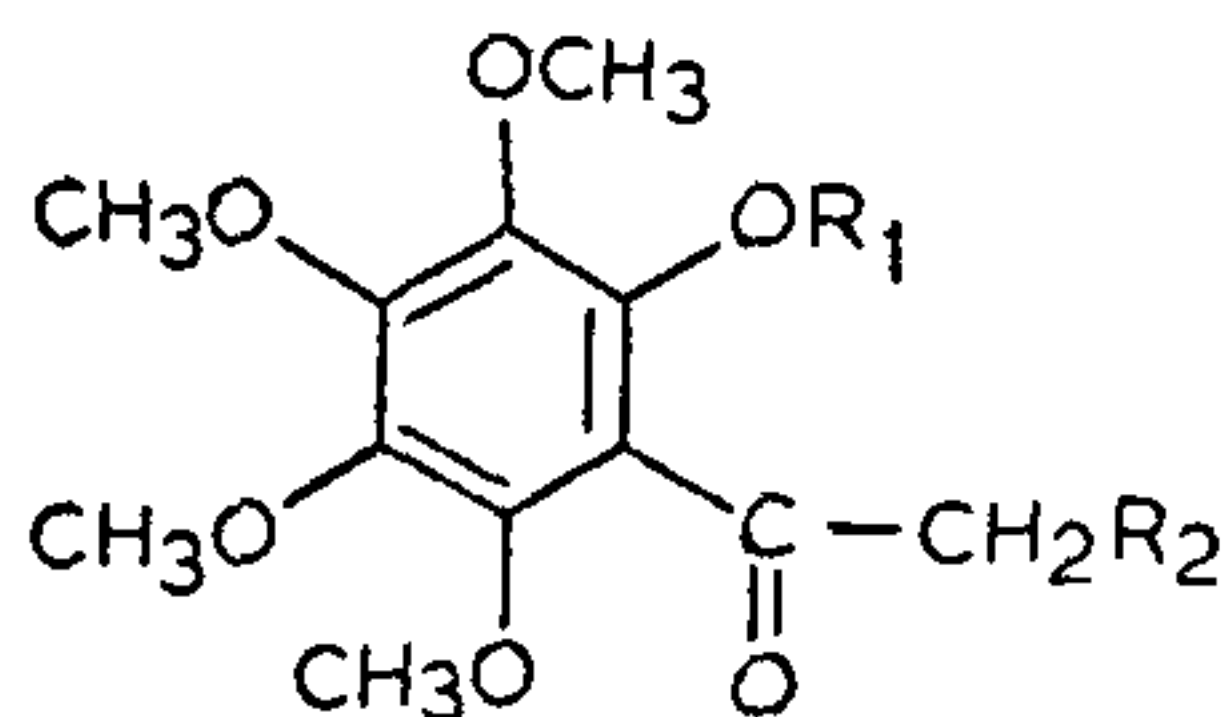
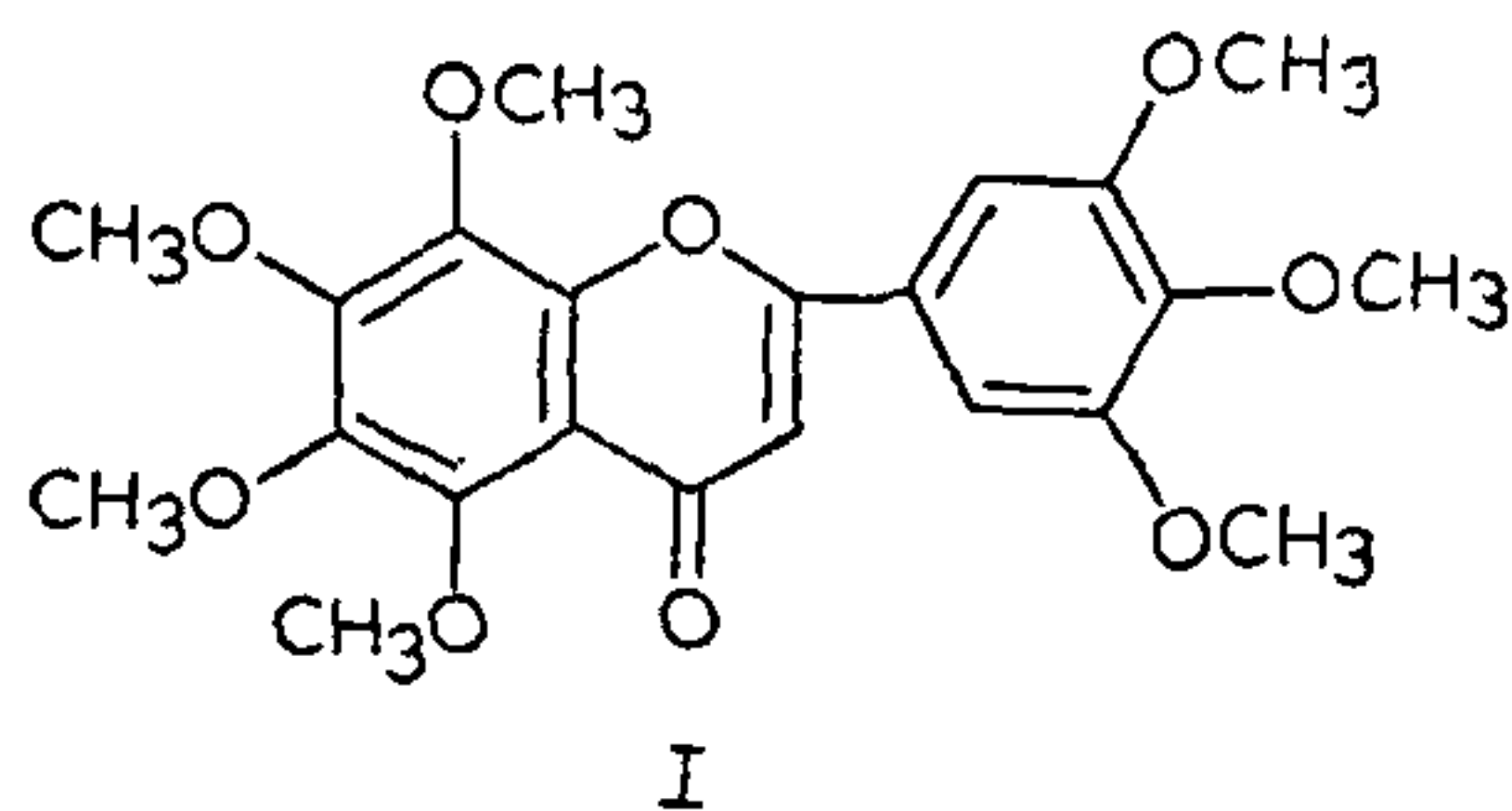
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## SYNTHESIS OF EUPATORIUM COELESTINUM FLAVONE

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CONSTITUTION assigned to a new flavone isolated from *Eupatorium coelestinum* as 5, 6, 7, 8, 3', 4', 5'-heptamethoxyflavone (I) has been now confirmed by its synthesis,



A new heptamethoxyflavone ( $\text{C}_{22}\text{H}_{24}\text{O}_8$ , m.p.  $102^\circ$ ) isolated from *Eupatorium coelestinum*, on the basis of colour reactions and spectral data was proposed its constitution as 5, 6, 7, 8, 3', 4', 5'-heptamethoxyflavone<sup>1</sup> (I). This communication confirms the proposed structure by synthesis. The flavone (I) has been now obtained using 2-(3', 4', 5'-trimethoxy)benzoyl oxy-2, 4, 5, 6-tetramethoxyacetophenone (III) prepared by the esterification of 2-hydroxy-2, 4, 5, 6-tetramethoxyacetophenone<sup>2</sup> (II) with tri-*o*-methylgalloyl chloride<sup>3</sup> in the presence of pyridine. The ester (III) underwent Baker-Venkataraman migration<sup>4,5</sup> to yield 2-hydroxy-3, 4, 5, 6, 3', 4', 5'-heptamethoxydibenzoylmethane (IV) which on cyclodehydration<sup>6,7</sup> gave 5, 6, 7, 8, 3', 4', 5'-heptamethoxyflavone (I).

The flavone (I) has also been obtained by another method using 2'-hydroxy-3, 4, 5, 3', 4', 5', 6'-heptamethoxychalcone (V) which itself was obtained from 2-hydroxy-3, 4, 5, 6-tetramethoxyacetophenone<sup>1</sup> (II)