

LETTERS TO THE EDITOR

EFFECT OF ANNEALING ON THE CATALYTIC ACTIVITY OF COPPER*

BHAKTA AND TAYLOR¹ have shown that gold catalyst, on annealing *in vacuo* in the temperature range of 200° to 400° C followed by quenching at liquid air temperature, acquired excess activity (towards the dehydrogenation of formic acid) which decayed out at a lower anneal temperature. The present investigation was undertaken to ascertain whether copper would also show a similar effect upon annealing in air for one hour at 250° to 550° C followed by either (a) quenching in water at 25° C, or (b) slow cooling in a furnace. The results revealed some unexpected interesting features. Square pieces (3.0 cm × 3.0 cm) of copper foils (99.9% purity, B.D.H.) from separate lots I, II and III, of mean thickness 0.10 mm, 0.12 mm and 0.13 mm, respectively, were used; the gm. equiv. of hydrogen peroxide (0.25 N) decomposed per unit surface area of the foil during the initial 10 min. of the reaction at 69.5° C at a stirrer speed of 200 rpm was taken as a measure of the activity, a , of the foil.

As the activity of the unannealed foils were found to be nearly proportional to the reciprocals of their thickness, mapping of the annealing data of the three foils on a single scale based on a_0 (1.58×10^{-4} gm. equiv. cm.⁻², the activity of the unannealed foil I) was possible. (Fig. 1).

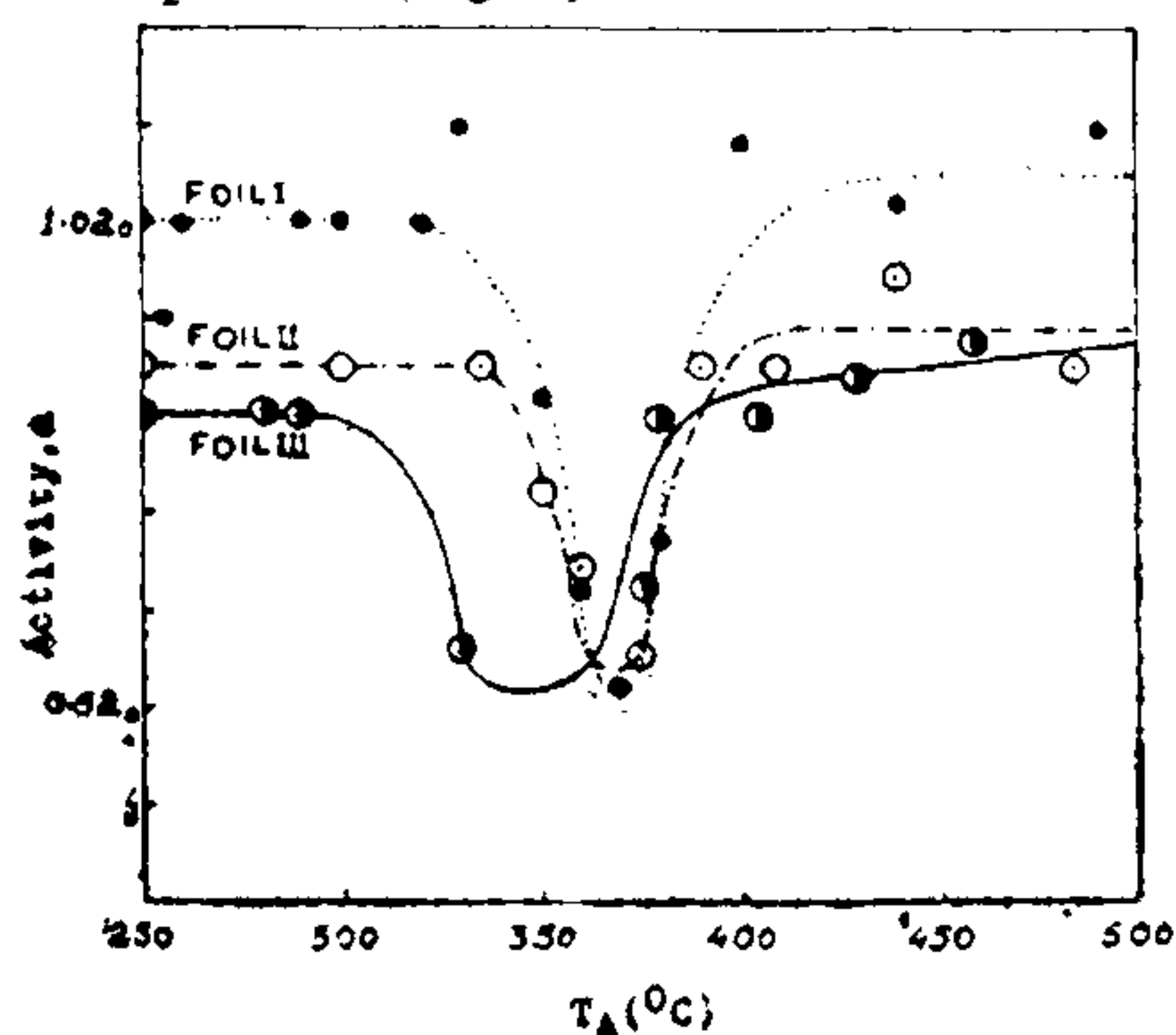


FIG. 1

This investigation has revealed that

A. the activities of the foils I, II and III.

- (i) remained, apparently, constant at their respective unannealed values (i.e., a_0 , $0.85 a_0$, $0.80 a_0$, respectively) upto $T_A \sim 300^\circ \text{C}$.

- (ii) attained the same minimum residual activity ($0.5 a_0$ approximately) in the same T_A range of 330°C to 380°C .

- (iii) showed similar trend of activity increase (following the minima) to reach once again values nearly equal to their respective unannealed ones, at about the same temperature range (380°C to 420°C) and remained practically constant at $T_A > 420^\circ \text{C}$.

- (iv) showed the same pattern of behaviour, viz., (i), (ii) and (iii) when the foils were furnace-cooled (instead of quenched) after annealing at T_A range 250°C to 550°C .

and

B. the Vickers microhardness of foil II remained unchanged upto $T_A \sim 420^\circ \text{C}$, thereafter it decreased to a final constant value (70% of the initial value) at $T_A \sim 480^\circ \text{C}$.

In passing, it can be noted that the onset of 'softening' of a foil began at about 420°C at which it attained the maximum activity. At the present moment it is not possible to say if this is a mere coincidence.

The activity decay in the T_A range 300°C to 380°C follows a pattern similar to that observed by Eley and MacMahon² and Uhara *et al.*³. The present investigation succeeds in clearly delineating the complete picture of the changes in the activity of the foils in the T_A range of 250°C to 550°C .

It seems likely that the free surface of the copper foil is itself active accounting for the unannealed activity ($0.5 a_0$). The activity of the foil in excess of $0.5 a_0$ may be attributed to the surface terminations of dislocations in accordance with the views of Cratty and Granato⁴; the annealing characteristics of its hardness are also consistent with these views. These dislocations are, perhaps, introduced in the foils when they were cold-rolled (during manufacture); as the thickness of a foil is, presumably, proportional to the amount of cold-work performed and, consequently, to the number of dislocations introduced, the reason for the observed dependence of the activity of a foil on the reciprocal of its thickness, becomes clear.

The rise in the activity following the minimum is, however, not easy to interpret. There is, undoubtedly, visible roughening of the surface of the foil after annealing at $T_A > 380^\circ \text{C}$. But this alone is not sufficient to account for the observed increase in the activity; nor can this increase be attributed

to the strains caused by quenching, as the quenched foils did not behave differently from the furnace-cooled ones. As every foil was first immersed in 2 N H_2SO_4 for 3 to 4 min. (until it regained its shine) before it was used as a catalyst, the probability that the oxide film on its surface might be responsible for the increase in activity, is small. Incidentally it is worth noting that silver catalyst, too, exhibited similar increase in activity³ when hydrogen peroxide decomposition and ethanol oxidation (and not formic acid dehydrogenation) were the probe reactions. This observation may be of significance to the understanding of the mechanism of metal catalysed reactions.

Department of Chemistry,
Dhempe College of Arts and
Science,
Panjim, Goa, August 27, 1974.

K. SAWKAR.
M. A. BHAKTA.

* This communication is based on the dissertation submitted by K. S. to the University of Bombay for the M.Sc. degree.

1. Bhakta, M. A. and Taylor, H. A., *J. Chem. Phys.*, 1966, 44, 1264.
2. Eley, D. D. and MacMahon, D. M., *J. Catalysis*, 1969, 14, 193.
3. Uhara, I., Kishimoto, S., Yoshida, Y. and Hikino, T., *J. Phys. Chem.*, 1965, 69, 880.
4. Cratty, L. E. and Granato, A. V., *J. Chem. Phys.*, 1957, 26, 96.

ELECTRONIC SPECTRAL AND THERMAL STUDIES OF Ce(III), Pr(III) AND Nd(III) PICRAMATES

SOME inner transition metal picramates, viz., lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, dysprosium and holmium picramates, were prepared recently by us and their stoichiometry established by elemental analysis, amperometric, conductometric and potentiometric

studies^{1,2}. We also suggested $-\text{H}_2\text{N} \rightarrow \text{Ln}$ coordination (Ln—rare earth ion) in metal picramates on the basis of i.r. spectral studies. The present communication reports the electronic spectral and thermal studies of cerium, praseodymium and neodymium picramates. The nature of the complexes has also been studied by measurements of electrical conductance.

The conductance and electronic spectra of the complexes were made as reported in the earlier communication³.

The low molar conductivity of the complexes in dimethylformamide showed that these complexes are non-electrolytes. The spectral data of praseodymium and neodymium picramates in ethanol are summarised in Table I, and for comparison, data for aqueous salt solutions are also given.

The spectral behaviour of lanthanides is fundamentally different from that of *d*-block elements. The basic reasons for the differences lies in the fact that the electrons responsible for magnetic spectral properties of lanthanide ions of 4*f* electron and 4*f* orbitals are effectively shielded from interaction with external forces by the overlapping of 5*s*² and 5*p*⁶ shells. The bands may be assigned to the transitions in which an *f* electron is excited to an outer *d*, *s* or *p* orbital⁴ and the spectra have been assigned to 4*f*-5*d* transitions⁵. The electronic spectra of the cerium picramate show five bands appearing at 21735 (vw), 23250 (vw), 31755, 44455 and 47660 cm^{-1} . The first three bands may be due to Laporte-allowed 4*f* \rightarrow 5*d* transitions.

It is evident from Table I that the shifts in the spectra of praseodymium and neodymium picramates are towards lower wave numbers relative to the aquo ions. There are small differences in frequencies or molar absorption except that the hypersensitivity transition $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{7/2}$ in the neodymium picramate which increases in intensity from $\epsilon = 6.25$ in the salt to $\epsilon = 17.50$ in the com-

TABLE I

Electronic spectra of praseodymium and neodymium nitrate and their corresponding complexes

Transition	Ln (NO_3) ₃ in water (cm^{-1})	ϵ salt	[Ln (C_6H_5) ₂ (NO_3) ₂ (NH_2O) ₃ ·2 H_2O] in ethanol (cm^{-1})	ϵ complex	ϵ complex
					ϵ salt
Pr	$^3\text{H}_4 \rightarrow ^1\text{D}_2$	17,000	16,860 (0.0083)*	2.60	1.36
	$\rightarrow ^3\text{P}_0$	20,750	20,700 (0.0024)*	3.55	1.18
	$\rightarrow ^3\text{P}_1$	21,320	21,140 (0.0085)*	11.76	2.80
	$\rightarrow ^3\text{P}_2$	22,470	22,430 (0.0017)*	10.89	2.09
$^4\text{I}_9$	$\rightarrow ^4\text{F}_{5/2}, ^2\text{H}_{9/2}$	12,500	12,450 (0.0040)*	11.90	1.85
	$\rightarrow ^4\text{F}_{7/2}, ^4\text{S}_{3/2}$	13,400	13,310 (0.0067)*	9.20	1.57
Nd	$\rightarrow ^4\text{G}_{5/2}, ^2\text{G}_{7/2}$	17,300	17,150 (0.0087)*	17.50	2.80
	$\rightarrow ^4\text{G}_{7/2}$	19,000	18,910 (0.0047)*	6.26	1.86
	$\rightarrow ^4\text{G}_{6/2}$	19,500	19,400 (0.0051)*	3.66	2.21

* Values in parentheses show the nephelauxetic effect (1- β).