CHARACTERIZATION OF CHEMISORBED ORGANIC RESIDUES

P. Sidheswaran

Indian Institute of Technology, Bombay

(Now at : Surface Chemistry Section, Hindustan Lever Ltd, Bombay)

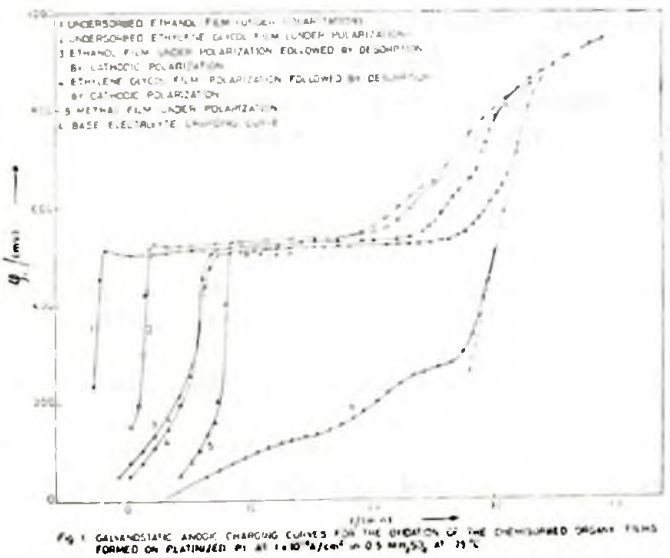
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The basic features which differentiate the CH-type organic species from the O-type organic species are described in this article.

Two types of chemisorbed residues on platinum group electrodes have been described in literature[1,2], the O-type (or the more oxidized type) and the CH-type (or somewhat relatively less oxidized type) residues. In a previous communication, the nature of the CH-type organic residues chemisorbed on platinized-platinum had been described[3]. In this article, the electrochemical nature of the O-type chemisorbed residues is presented with its basic distinctions from the CH-type residues.

What are the O-type and CH-type residues ?

The chemisorbed organic films were first formed on the platinized-platinum electrode with different organic adsorbates using the procedure described elsewhere[1,4,5]. The anodic galvanostatic charging curves obtained for the oxidation of the films of ethanol, ethylene glycol and methanol formed under different conditions are presented in Fig. 1. In the case of the chemisorbed films of



methanol, formaldehyde, formic acid, glyoxal and 'reduced CO_2' at the higher potential (ϕr) range (between 550 to 850 mV) the rise of ϕr is sharper with time. However, in the case of ethanol, and ethylene glycol, a slow rise of potential is registered in the same potential span and the species getting oxidized in this range has been assigned a non-committal name the CH-type residue. Even after desorption a portion of the CH-type residue existed in the cases of ethanol and glycol (Fig. 1).

The characteristic differences between the O-type and the CH-type residues (Table. 1).

a) **Extent of desorption :** When the chemisorbed films of ethanol and glycol, were cathodically polarized, there was a significant desorption of the residues. This was arrived at from the fact that the adsorption coefficient, K* (= QM QSH), fell from 1..5 (undesorbed film) to about 0·75 (desorbed film), in the case of open circuit film[6]. Even the film formed under steady state polarization got desorbed by cathodic polarization. With the open circuit or steady state film of ethylene glycol also, there was significant desorption as noticed in the case of ethanol film[7].

Table. 1. Diagnostic Chemisorption Parameters.

	Distinguishing parameter	O-type residue	CH-type residue
(1)	(e)	= 1	larger than 1.
(2)	QM/QCO_2	≅ 1	larger than 1.
(3)	$QM/\Delta QH$	smaller	larger
(4)	QM at elevated temperatures	No desorption	Significant desorption
(5)	Tafel slope	∾70 mV	∼110 mV
(6)	formation of intermediates of the reaction	not formed	formed
(7)	Shape at lower organic coverages.	Steep rise	Slow rise of ϕr.
(8)	residual current after the oxidation of residue.	nil ($\sim$ 0)	Significant.

Similar desorption behaviour was registered with ethanol[6,8] and glycol[7].

In the case of chemisorbed films of methanol, formic acid, formaldehyde, and 'reduced CO_2', our trials to desorb the film both by cathodic polarization and by hydrogenative desorption were unsuccessful because these carbonaceous films were very tenacious and remained undesorbable. They could be desorbed only

*QM is the charge spent in oxidizing the chemisorbed organic residue and QSH is the charge spent in oxidizing a mono-layer of adsorbed hydrogen present on the platinized-platinum electrode.

by the usual oxidative reaction by the application of an anodic current. This strongly suggested that the film containing CH type residue alone could be desorbed, whereas only negligible desorption occurred with the O-type residues.

(b) **Diagnostic Chemisorption Parameters**

The four important diagnostic parameters utilized for the elucidation of the structure of the chemisorbed residues were described elsewhere[8,9]. They could be very useful in determining the type of residue also.

(1) The electrons per site ratio (e)

It has been defined as the ratio of the oxidation state of the chemisorbed residue to the number of sites occupied by the residue. Hence the value of (e) for CO or CHO was found to be one whereas for CH_3 it should be theoretically 7. It has been noticed that (e) $\simeq$ 1 for the O-type residues whereas it was greater than unity for the CH-type residue.

If $K > 1.25$ invariably the existence of CH-type layers (from the shape) was noticed. The O_u (surface bareness) vs K plot for ethanol in 0.5 M H_2SO_4 (Fig. 2) illustrates this view. Oxidation of the separated O-type residues alone gave a K_{max} (Fig. 2) of 1.0 whereas with the complete chemisorbed ethanol layer, $K \simeq .3$

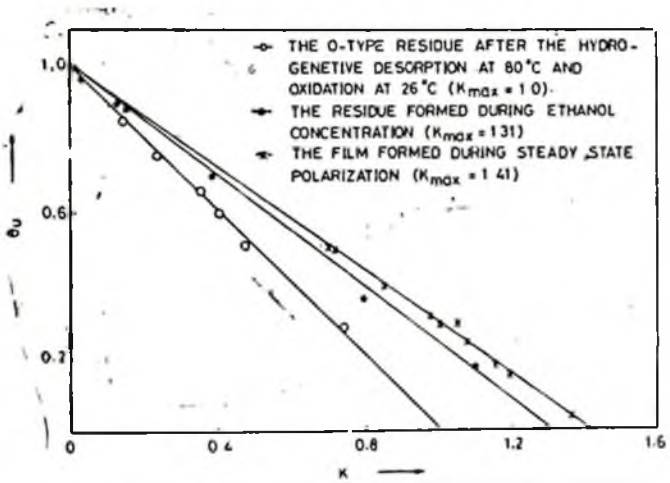


Fig 2 THE SURFACE BARENESS (θ_u) Vs ORGANIC SURFACE COVERAGE IN 0.5 M H_2SO_4

(2) QM/QCO_2 ratio

Since the CH-type residue is somewhat less oxidized in comparison with the O-type residue, the amount of charge spent in oxidizing the organic, QM, for the CH-type residue should be larger than that for the O-type species QCO_2 is the amount of CO_2 produced during the oxidation of the organic residue. QCO_2 was same for all the one carbon atom adsorbates (when all the sites were chemisorbed) in the case of both CH-type and O-type residues. However, the ratio QM/QCO_2 should be significantly larger for the CH-type species than in the case of the O-type residue.

(3) $QM/\Delta QH$ ratio

The O-type residue being more oxidized, for its further oxidation less charge is required in comparison with that for the CH-type residue.

(4) The Tafel slope

The Tafel slope for the oxidation at constant organic coverages could be different for different species. as in the case of chemisorbed ethanol. At lower organic coverages and higher potential regions ($\simeq$ 550 L 850 mV), where the CH-type residue got oxidized, the Tafel slope was higher ($\simeq$ 110 mV) whereas in the O-type region, about 70 mV was noticed.

(e) **Exposure to High Temperatures.**

In the case of the O-type residues, if the films were exposed to higher temperatures the adsorption coefficient remained the same. However, in the case of the open-circuit ethanol film, as the temperature of the system is increased from 25° to 80°C, a drop in K was noticed. This strongly suggested the existence of surface mobility at elevated temperatures. If CH-type radical has to hop on the electrode there should be monovaten platinum–carbon binding as in $Pt\text{-}CH_3$. Alkyl radicals having lesser platinum-carbon binding possessed remarkable desorbability and hence dimerized. Ethane was identified[1,10] by GLC studies and this demonstrated that CH_3 was the likely C-type residue which possessed both mobility and desorbability.

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