

Organic Adsorption at Electrodes

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Abstract: A review of the methods used to investigate the adsorption of organic compounds on solid metal electrodes shows that all of the available methods have very definite limitations. In the absence of a really good method, it is wise to employ all the available techniques which give complementary information.

The available experimental information obtained from electroadsorption measurements is compared with the data obtained from gas-phase studies. As an example of the difficulty encountered in making a comparison of gas-phase and electroadsorption measurements, it is found in the study of adsorption energetics that the heats of adsorption are much lower in electroadsorption. When water vapor is present, electroadsorption is most likely similar to competitive gas-phase adsorption. A discussion of the energetics of adsorption clearly shows the competitive nature of adsorption at electrodes in solution.

The adsorption characteristics of carbon monoxide, formic acid, methanol, ethanol, and hydrocarbons, especially ethylene, are discussed in some detail.

A review of adsorption phenomena observed at open circuit shows that when a steady potential is established at platinumized Pt electrodes in solutions of alcohols and aldehydes containing more than one carbon atom, processes of dehydrogenation and self-hydrogenation of the original substances and their decomposition products occur.

INTRODUCTION

The types of information required for a discussion of adsorption of gases at metal surfaces have been enumerated by Bond (1). With minor variations, similar information is desired from the measurements of adsorption of organic compounds on solid metal electrodes. This information includes:

1. the conditions of adsorption—under what conditions of temperature, pressure or concentration, *etc.*, and on which metals does the compound in question chemisorb;

2. the stoichiometry of the adsorption process— is chemisorption associative or dissociative, how many sites are involved for the adsorption of one molecule, is the adsorbed species mobile on the surface, what is the nature of bonding;

3. the energetics of adsorption—the equilibrium constant and its temperature variation, free energy, heat and entropy of adsorption, their variation with coverage, the activation energy for

adsorption and desorption, and the strengths of the bonds involved in the adsorption process;

4. the adsorption isotherm—the variation of coverage with pressure or concentration, temperature, potential, solvent, and pH; and

5. the kinetics of adsorption—the rates of adsorption and desorption.

With the only-recently-developed interest in adsorption at solid metal electrodes, it should be obvious that very little of this information has been obtained for even one system. As a matter of fact, the desired information is far from complete for even a single system in gas-phase adsorption (1,2). Therefore, any discussion of organic adsorption at solid electrodes must necessarily be incomplete with respect to experimental evidence and information. In the next section we shall present much of the available data on the electroadsorption of organic compounds, although no attempt is made at completeness. Information from adsorption on mercury, recently reviewed by Frumkin and Damaskin (3), and gas-phase adsorption are presented where comparison seems justified.

COMPARISON OF METHODS FOR ADSORPTION STUDIES IN THE GAS PHASE AND AT ELECTRODES IN SOLUTION

The experimental methods for the study of electroadsorption have been reviewed for equilibrium

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TABLE I
Methods for the Study of Adsorption

Gas Phase	Solid Electrodes in Solution
1. Volumetry and gravimetry	1. Coulometric: galvanostatic charging, galvanostatic hydrogen deposition, potential sweep, chronopotentiometry
2. Accommodation coefficients	
3. Magnetic susceptibility	2. Differential double-layer capacity
4. Specific magnetization	3. Radiotracer: isotope-labelling detection in solution or on the electrode
5. Work function changes	
6. Electrical conductivity	4. Spectrophotometric: change in solution absorption of uv
7. Kinetic studies— isotopic traces	5. Ellipsometry
8. Infrared spectroscopy	
9. Gas-solid chromatography	
10. Electron spin resonance	
11. Field ion microscopy	
12. Field emission microscopy	
13. Low-energy electron diffraction (LEED)	
14. Flash desorption	

adsorption (4) and for adsorbed intermediates (5). Methods applicable in gas-phase studies have been reviewed by Bond (1) and by Hayward and Trapnell (2), and modern techniques are discussed by Ehrlich (6). The fundamental difference of the solution phase presents severe limitations on the experimental approach to electrosorption, and many of the exciting techniques now being utilized in the gas phase are simply not applicable. Table I lists the various methods which can be used to study adsorption in the gas phase and at electrodes in solution. In gas-phase study, tremendous advances have been made due primarily to the development of ultrahigh vacuum techniques. For the first time it has become possible to specify exactly the environment at an interface and to perform meaningful measurements on samples with small surface areas (6). The use of high vacuum has permitted the use of the field emission microscope, which can scan the surface on a scale

that approaches the realm of atomic dimensions, and the field ion microscope, which gives an even greater resolution. In many cases new problems arise in the study of clean systems. The structural studies of clean surfaces with low-energy electron diffraction (LEED) have caused more problems than they have solved (7), and at present adsorption is being investigated before the clean surfaces themselves are understood.

For the study of adsorption two requirements should be met: both the metal surface and adsorbing species must be in known reproducible states, and the environment must be adjusted to prevent introduction of impurity. The speed of contamination of clean metal surfaces has been realized for some time in gas-phase studies (8). In the gas phase the time τ for 1% contamination of the metal surface, assuming that one out of every four molecules striking the surface will stick, is given by (6)

$$\tau = (10^{-7}/p) \text{ sec.}$$

Thus at a pressure p of 10^{-6} torr, 100 msec are available for experimentation with a metal surface less than 1% contaminated. The above requirements have been fairly well met in a few studies by the use of ultrahigh vacuum techniques, and the problem is now well understood for gas phase adsorption measurements.

The study of adsorption in solution presents somewhat more of a problem. Although the influence of impurity was realized by Frumkin's school in the 1930's, and reemphasized by Bockris and coworkers, acceptable conditions of purity have not in general been maintained in electrochemical systems. A recent and rather unfortunate trend in electrochemical measurements has been to substitute transient methods and electrode pretreatment sequences for the design and maintenance of clean systems. Just as gas-phase studies required the development of the Bayard-Alpert inverted ionization gauge to measure pressures in ultrahigh vacuum systems, perhaps methods for testing the purity of solution and electrode cleanliness are required before consistent and meaningful measurements at electrodes in solution are made. A step in this direction has been made by Schuldiner and Warner (9), who have suggested a simple method for determining the cleanliness of a platinum anode. Using the equivalent of high-vacuum techniques (electrochemical measurements in solution can never approach ultrahigh vacuum techniques for obvious reasons), it has been possible to maintain highly clean systems for periods of several months (10). These results show that with proper system design and a little effort, electrochemical measurements can be made in clean systems reproducibly without resorting to techniques which act as substitutes for system purity. Thus the design and operation of clean electrochemical systems would seem to be a prerequisite before reproducible, and indeed meaningful, information on electrosorption of organic compounds can be obtained. The often-heard argument that the organic species being examined is itself an impurity, and therefore system cleanliness is impossible, is not relevant.

The question of which method is best for the study of electrosorption may be simply answered by stating that all of the available methods have very definite limitations, and in the absence of a

really good method, it is wise to employ all of the available techniques which give complementary information. The experimental problems involved in radiotracer techniques are relatively greater; however, the results are more easily interpreted in terms of the total amount of species formed and are based on fewer assumptions than are the various electrochemical methods. Other methods have been attempted, *e.g.*, infrared spectroscopy using internal reflection and electron spin resonance (11), but with little success. Electrosorption is still awaiting the development of a good *in situ* method of examining adsorbed layers at metal surfaces.

ENERGETICS OF ADSORPTION

The intention of this section is to compare the thermodynamic quantities determined for the adsorption of selected compounds in the gas phase with those for the electrosorption of the same species. This comparison is at best difficult since gas-phase studies have in general determined the heat of adsorption primarily from calorimetric measurements or from isotherms using the Clausius-Clapeyron relation, while the few studies of electrosorption which have considered the energetics have determined free energies from isotherms. Heats of adsorption have been determined at platinum electrodes for ethylene (12) and benzene (13) from the variation of equilibrium constant, determined from the adsorption isotherms, with temperature using the Van't Hoff equation. However, the adsorption of these compounds on platinum in the gas phase has not been reported. Hydrogen adsorption, which has been extensively studied in the gas phase (2) on a number of metals, has been examined at Pt, Rh, and Ir electrodes by Breiter (14) using the technique of cyclic voltametry to obtain free energy, heat, and entropy of adsorption. While this is not organic adsorption, it can give an indication of the differences in gas-phase processes and electrosorption. Heats in the gas-phase range from -45 kcal/mole on tungsten to -26 kcal/mole on palladium and -28 kcal/mole on rhodium (2). On platinum and rhodium, Breiter has obtained heats of adsorption of about -18.5 kcal/mole at zero surface coverage ($\theta = 0$) and from -8.5 to -13.0 kcal/mole for a coverage of $\theta = 0.5$. These values tend to show that the heats of adsorption on

TABLE 2
Comparison of Heats of Adsorption
from Gas-Phase and Electrosorption Measurements

Metal	Gas Phase (kcal/mole)			Electrosorption (kcal/mole)		
	H ₂ (Ref. 2)	CO (Refs. 1 and 2)	C ₂ H ₄ (Refs. 1 and 2)	H ₂ (Ref. 14)	C ₂ H ₄ (Ref. 12)	C ₆ H ₆ (Ref. 13)
W	-45	-82	-102	-	-	-
Ni	-30	-42	-58	-	-	-
Fe	-32	-46	-68	-	-	-
Rh	-28	-	-50	-18.5	-	-
Pd	-26	-	-	-	-	-
Pt	-	-	-	-18.5	0	+10
Cu	-	-9	-19	-	-	-
Au	-	-9	-21	-	-	-

electrodes in solution are in general much less than those in the gas phase, which is to be expected for the replacement reaction (15). Limitations on the quantities determined by Breiter have been discussed by Frumkin (16) so that these values should be used with caution. In addition, Breiter has assumed the Nernst relation to determine the partial pressures of hydrogen from electrode potentials. This assumption has been shown not to be valid below 10^{-6} atm hydrogen partial pressure (10), because of hydrogen absorbed in the Pt, and becomes invalid at somewhat higher partial pressures in the presence of oxygen (17).

Table 2 shows the difficulty in making a comparison of gas-phase and electrosorption measurements. In general, the heats of adsorption are much lower in electrosorption. This has been explained by the fact that electrodes are covered with water molecules and energy is required to displace them from the surface. The idea that electrosorption is a replacement reaction is more clearly brought out by examining the free-energy quantities determined for the adsorption of a number of organic species at electrodes.

The net free energies of adsorption $\Delta\bar{G}_a^0$, defined as (18)

$$\Delta\bar{G}_a^0 = (\bar{\mu}_A^{0,a} - \bar{\mu}_A^{0,s}) - n (\bar{\mu}_{H_2O}^{0,a} - \bar{\mu}_{H_2O}^{0,s}),$$

are given for a number of butyl, phenyl, and naphthyl derivatives in Table 3. Here $\bar{\mu}_A^{0,a}$ and

TABLE 3
Net Free Energies of Adsorption $\Delta\bar{G}_a^0$ of
Butyl, Phenyl, and Naphthyl Derivatives
on Hg (18) (0.1N HCl, potential at electro-
capillary maximum surface coverage
 $\theta = 0.25$)

Functional Group	$-\Delta\bar{G}_a^0$ (kcal/mole)		
	N-C ₄ H ₉	C ₆ H ₅	C ₁₀ H ₇
OH	3.7	5.6	8.8
CHO	6.5	6.6	9.0
COOH	4.5	6.7	8.6
CN	4.5	6.0	-
NH ₃ ⁺	2.9	3.9	7.3
SH	4.9	7.5	-
SO ₃ ⁻	2.6	3.8	7-7.5
CO	~8	-	-

$\bar{\mu}_{H_2O}^{0,a}$ are the standard electrochemical potentials of adsorbate and water in the adsorbed state, referred to unit mole fractions on the metal surface, $\bar{\mu}_A^{0,s}$ and $\bar{\mu}_{H_2O}^{0,s}$ are the standard electrochemical potentials of adsorbate and water in solution, referred to unit mole fractions in the solution, and n is the number of water molecules replaced, determined on mercury by the electrocapillary method.

The standard electrochemical free energy of adsorption, as obtained from the Langmuir isotherm in the form

TABLE 4
Comparison of Free Energies of Adsorption $\Delta\bar{G}^0$ of Organic Bases and Their Conjugate Acids on Hg (19) (potential -600 mv vs S.C.E., 26°C)

Adsorbate	$-\Delta\bar{G}^0(\text{kcal/mole})$ ($\theta = 0.5$)	1N HCl ($\theta = 0.25$)	$-\Delta\bar{G}^0(\text{kcal/mole})$ ($\theta = 0.5$)	1N KCl ($\theta = 0.25$)
pyridine	2.5	4.8	3.3	—
2-NH ₂ -pyridine	4.5	5.3	4.0	—
2-Cl-pyridine	3.5	5.6	5.3	5.9
1,2,3,6-tetrahydra- pyridine	3.7	4.6	4.5	—
piperidine	3.6	4.3	4.6	—
aniline	4.1	—	4.5	—

TABLE 5
Standard Free Energies of Adsorption at Potential
of Maximum Adsorption as $\theta \rightarrow 0$

Metal	$-\Delta\bar{G}^0$ (kcal/mole)				
	Naphthalene* (Ref. 20)	n-decylamine† (Ref. 20)	Ethylene‡ (Ref. 12)	Benzene‡	Cyclohexane‡ (Ref. 22)
Ni	6.0	6.8	—	—	—
Fe	7.0	6.6	—	—	—
Cu	7.0	7.3	—	—	—
Pd	—	6.2	—	—	—
Pt	8.4	7.4	5.6	5.7-8.7 (Ref. 13)	—
Au	0.7‡ (Ref. 22)	—	—	6.1 (Ref. 22)	< 5.8

*1N NaClO₄.

†0.9N NaClO₄; 0.1N NaOH.

‡1N H₂SO₄.

$$\frac{\theta}{1-\theta} = \frac{C_A}{55.5} e^{-\Delta\bar{G}^0/RT},$$

has been determined for the adsorption of several organic bases and their conjugate acids on mercury (19) and are presented in Table 4.

Finally, the standard free energies of adsorption for ethylene and benzene as determined from equilibrium constants (12,13) and for n-decylamine and naphthalene as determined from the isotherm (20,21)

$$\frac{\theta}{(1-\theta)^n} \frac{[\theta + n(1-\theta)]^{n-1}}{n^n} = \frac{C_{org}}{55.5} e^{-\Delta\bar{G}^0/RT},$$

which reduces to the usual Langmuir isotherm when n , the number of water molecules displaced by one organic molecule on adsorption, becomes

equal to one, are given in Table 5 for solid metal electrodes.

It is readily apparent that the standard free energies of adsorption of a wide variety of organic compounds on a number of solid metal electrodes and on mercury are quite similar, with a variation of less than 10 kcal/mole, and in most cases less than 5 kcal/mole. This leveling effect in electroadsorption is thus a good indication of the strong influence of solvent molecules in determining adsorption energies. There are also some indications that the presence of water vapor in gas-phase adsorption can have large effects on the heats of adsorption (1,2). The effect of the adsorption of water vapor on contact potentials has been known for some time, and particularly large effects are obtained in critical ranges of water vapor below

competition model, as due to the slightly preferred orientation of water molecules with oxygen toward the metal surface at the p.z.c. From some measurements on Hg, where the p.z.c. is well established, there are good indications that the adsorption maximum is on the negative side for aliphatic molecules, but on the positive side for aromatic molecules (18). The p.z.c. was displaced to positive values by the adsorption of aliphatic compounds and to negative values by aromatics. This shift in p.z.c. is due to the substitution of organic molecules for water dipoles. From adsorption studies of aromatic and cyclic bases, it was reported (19) that no sharp maximum in adsorption near the p.z.c. is observed as compared with aliphatic species. The suggestion that this was not related to the π -orbital character of the rings was made because hydrogenated derivatives of pyridine maintained the tendency.

The shift of the p.z.c. in a negative direction and the adsorption of aromatic compounds on positively charged Hg surfaces is attributed to π -electron interaction, which is facilitated by the flat orientation of the benzene ring. Neutral organic molecules, which do not contain π -electrons, were not found to adsorb on Hg at large positive surface charges. Adsorption on positive surfaces was found to increase as the number of double bonds or π -electrons increased. A comparison of electrocapillary curves measured in solutions of organic substances forming an homologous series showed that the decrease in interfacial tension, and consequently the adsorption at identical concentrations, increases with an increase in chain length. Adsorption increases with the increasing concentration of solute and also with the concentration of the supporting electrolyte. This latter effect has been attributed to a salting out effect and not to adsorption of inorganic ions. Adsorption is strongly reduced by competitive adsorption of anions. Surface-active ions can either increase or decrease organic adsorption. The adsorption of anions decreases adsorption of neutral molecules, but it can increase the adsorption of organic cations by decreasing the mutual repulsive forces on the surface. From an examination of the simultaneous adsorption of n-butyl alcohol and tetraalkylammonium cations, it was found that desorption of the alcohol was less pronounced with the larger cations, being in the sequence $K^+ > (CH_3)_4N^+ > (C_2H_5)_4N^+ > (C_4H_9)_4N^+$.

From electrocapillary measurements it can be concluded that, in general, aliphatic organic molecules are oriented perpendicular to the metal surface, while aromatic molecules are oriented parallel, *i.e.*, adsorbed flat, on the metal surface. In neutral solutions, the values of limiting adsorption for aniline, pyridine, and their derivatives correspond to an orientation of adsorbed dipoles perpendicular to the surface. Butyl derivatives were found to adsorb perpendicular with the hydrocarbon end of the molecule toward the metal (18). However, it has been reported that for aliphatic oxygen compounds the molecule is oriented with the hydrocarbon end toward the interface and the negative end toward the metal (3). Obviously, the orientation of the dipoles will generally depend on the charge on the metal surface. It has also been proposed that the orientation will depend on the charge; *e.g.*, the vertical orientation of molecules, which is characteristic of negatively charged surfaces, can be substituted by a horizontal one, in which case the π -electrons of an aromatic ring can interact with the positive charges of the Hg surface.

In terms of energy changes, the standard free energy of adsorption was found to change symmetrically about the p.z.c. for some organic species, *e.g.*, ethylene, but to change unsymmetrically for others, *e.g.*, aromatic bases, where ΔG_{ads}^0 was lower at more anodic potentials. In general, the free energy increases with coverage, *i.e.*, becomes more negative, on negatively charged surfaces, and it decreases with increasing coverage on positively charged electrode surfaces. Conway (19) was able to obtain a linear correlation of ΔG_{ads}^0 with $\theta^{3/2}$, but with sharp inflections which were attributed to reorientation of dipoles as θ increased and to condensing of the dipole film.

A comparison of differential capacity curves in the presence of organic species shows a similarity in the first approximation of those obtained on solid metals to those obtained with Hg. A decrease in double-layer capacity with adsorption is observed, and the organic specie is seen to desorb with increasing electrode charge. The peaks on the capacity-potential curves were less pronounced on solid metals than on Hg. With an increase in chain length of the adsorbing organic molecule, the double-layer capacitance is observed to decrease due to an increase in thickness of the double layer.

In terms of isotherms, it has been suggested that the Temkin isotherm is but of limited applicability to the adsorption of neutral organic molecules (3). This statement is supported by the fact that the changes in energies and heats of electrosorption are relatively small, being on the order of a few kilocalories per mole. This point concerning the applicability of the Temkin isotherm to organic adsorption at electrodes has been further treated in this light (29).

A number of trends are also readily available from adsorption studies in the gas phase. For example, alkynes and dienes are generally very strongly adsorbed on all metals, and it is assumed that these are π -bonded to the surface. Metals which form ethylene complexes will also form complexes with other olefins, and vice versa. The extent of olefin isomerization and exchange is always characteristic of the metal and substantially independent of molecular weight. In addition, correlations have been made between the organometallic chemistry of transition metals and their adsorption properties and catalytic chemistry (25). For example, π -olefin complexes are formed by virtually all group-eight metals and the strength of olefin-metal bonds may vary considerably depending on other ligands present in the complex. All these metals adsorb olefins and are active in olefin hydrogenation. Both in catalytic and organometallic chemistry, an acetylene molecule can displace an olefin molecule unless the latter is either adsorbed at a metal surface or functioning as a ligand in a complex. In general, such correlations are not as easily applicable to electrosorption as, for example, are the trends in adsorption on Hg, and so these will not be further discussed. It would be very instructive to compare such trends in gas-phase adsorption obtained in the presence of water vapor, *i.e.*, under conditions of competitive adsorption which apply in electrosorption, but unfortunately such information is not available.

MODES OF ADSORPTION AND STRUCTURE OF ADSORBED SPECIES

Although a relatively large number of studies recently have been concerned with organic adsorption at solid electrodes, the information obtained has in general been rather meagre. Table 7 gives a fairly complete listing of systems

which have been studied and the experimental methods used. In general, the aim has been to obtain coverages using coulombic methods which are subject to several limitations. The information on coverages has been discussed elsewhere (4) and will be reviewed only briefly here for completeness. The aim in this discussion will be to examine information concerning the adsorbed species and the comparison with relevant gas-phase studies. This can best be accomplished by dividing the information into two sections: (a) that resulting from the usual adsorption studies, particularly from radiotracer measurements, and (b) that resulting from studies (83) of dehydrogenation, hydrogenation, *etc.*, at open circuit.

THE ADSORPTION CHARACTERISTICS OF SOME SELECTED COMPOUNDS

Carbon Monoxide

Carbon monoxide chemisorbs on Pt from aqueous solutions to essentially full coverage between 0.4 and 0.9 V_{NHE} , the coverage falling off rapidly to zero at about 0.91 V. An indication of the strength of the Pt-CO bond is obtained from the fact that chemisorbed CO is not displaced by hydrogen even at potentials negative to 0.0 V_{NHE} . Carbon monoxide remains adsorbed at a full monolayer even after essentially all traces of CO have been removed from solution. Using transient techniques, Gilman was able to distinguish between two types of adsorbed CO species which he termed linear, or one-site, and bridged, or two-site, adsorption following evidence for these two species from infrared spectroscopy measurements in the gas phase. An examination of the gas-phase and catalysis literature on CO adsorption should permit a better understanding of the types of bonding involved. However, with the larger amount of information available, the situation for CO adsorption in the gas phase is in perhaps a considerably more confused state. Eischens and Pliskin (84) have given a fairly complete discussion of CO adsorption studies in the gas phase using infrared spectroscopy from which the linear and bridged forms of adsorbed CO were suggested. In more recent studies of CO adsorption on Ni using infrared techniques, Blyholder (85) found strong absorption bands at 1940 and 2080 cm^{-1} and a medium band at

TABLE 7
Information Concerning Electrosorption of Organic Compounds on Solid Metal Electrodes

System	Electrolyte	Temp. (°C)	Information Obtained	Method*	Ref.
CO, Pt	1M H ₂ SO ₄	25	Q at open circuit	A	30
CO, Plat. Pt	1N H ₂ SO ₄	15-50	Q as $f(V, T)$	A	31
CO, Pt	1N HClO ₄	20	Γ as $f(V)$	B	32
CO, Pt	1N HClO ₄	30	θ as $f(V)$	B	33
CO, Pt	1N HClO ₄	40	Q, θ_H or $f(V)$	A,C	34
HCOOH, Pt	1N HClO ₄	30	θ as $f(V, \text{conc})$	A,C	35
HCOOH, Pt	1M HClO ₄ + NaOH	40	θ as $f(V)$	A,C	36
HCOOH, Plat. Pt	5N H ₂ SO ₄	25-90	θ as $f(V)$	C	37
HCOOH, Pt	1N HClO ₄	40	θ as $f(V, \text{conc})$	A	38
HCOOH, Plat. Pt	1M H ₂ SO ₄	25	Q	B	39
HCOOH, Pt	1N HClO ₄	25	θ as $f(\text{Time}, \text{conc})$	B	40
CH ₃ OH, Pt	1N NaOH	25	θ as $f(\text{conc})$	A	41
CH ₃ OH, Pt	1N HClO ₄	25	θ as $f(V, \text{conc})$	B,C	42
CH ₃ OH, Pt	1N HClO ₄	25	Rate of adsorb.	B	43
CH ₃ OH, Pt, Ir, Au, Pd, Rh	1N HClO ₄	30	Capacity as $f(\text{conc})$	B	44
CH ₃ OH, Plat. Pt	0.1N H ₂ SO ₄	?	Q as $f(V)$ open circuit	A	45
CH ₃ OH, Plat. Pt	H ₂ SO ₄ , KOH	?	Q as $f(\text{pH})$	A	46
CH ₃ OH, Plat. Pt	0.1N H ₂ SO ₄	20	θ as $f(V)$	B	47
CH ₃ OH, Plat. Pt	1N H ₂ SO ₄	?	Q	A	48
CH ₃ OH, Pt	1N H ₂ SO ₄	25	θ as $f(V, \text{conc})$	D	49
CH ₃ OH, Plat. Pt	H ₂ SO ₄ , KOH	20	Q as $f(\text{pH})$	A,B	50
Pt-Ru, Pd-Ru, CH ₃ OH, Plat. Pt	H ₂ SO ₄ , KOH	20	Q as $f(\text{pH})$	A	51
CH ₃ OH, Pt	1N H ₂ SO ₄	25	Q	A,B	52
CH ₃ OH, Pt-Ru	H ₂ SO ₄ , KOH	20	Q as $f(\text{pH})$	A	53
C ₂ H ₅ OH, Plat. Pt	1N H ₂ SO ₄	?	Capacity as $f(V, \text{conc})$	E	54
C ₂ H ₅ OH, Plat. Pt	0.1N H ₂ SO ₄	20	Q as $f(V, \text{conc})$	A,B	55
C ₁ -C ₅ alcohols, Au	1N HClO ₄	5-25	Capacity as $f(V)$	F	56
allyl alcohol, allyl methanol, acrolein, methacrylic acid } Pd	H ₂ SO ₄ , KOH	?	Q	C	57
CH ₂ CHCH ₂ OH, Plat. Pt	0.1N H ₂ SO ₄		Q, capacity as $f(\text{conc})$	A,C	58
Butane-1-4-dial and derivatives } Pt	?	?	Q, Γ	A	59
(COOH) ₂ Au	H ₂ SO ₄	?	Film thickness	G	60
pyridine, acridine, quinoline, poly-vinylpyridine } Cu, Ag, Ni	Aq. and methanol	25	θ or $f(\text{conc})$	H	61
Hydroquinone, phenylenediamine, methylaminophenol } Ag	Na ₂ CO ₃	20,40	θ as $f(\text{conc})$	H	62
thiourea, Au	H ₂ SO ₄ -Na ₂ SO ₄	25	θ or $f(\text{conc})$ energetics	I	63

*A—anodic galvanostatic charging; B—linear anodic potential sweep; C—cathodic galvanostatic charging; D—linear cathodic potential sweep; E—ac impedance; F—differential capacitance from galvanostatic pulse; G—ellipsometry; H—uv absorption in solution; I—radiotracer; J—volumetric; and K—potential decay.

(Table Continues)

TABLE 7 (Continued)
Information Concerning Electrosorption of Organic Compounds on Solid Metal Electrodes

System	Electrolyte	Temp. (°C)	Information Obtained	Method*	Ref.
amyl alcohol } caprylic acid } Pt diphenylamine }	1M HClO ₄	?	Capacity as $f(V, \text{conc})$ θ as $f(V, \text{conc})$	B,E	64
C ₂ H ₄ , Pt	1N NaOH	60	Γ as $f(V, \text{time})$	I	65
C ₂ H ₄ , Plat. Pt	1N H ₂ SO ₄	25	Q	B	66
C ₂ H ₄ , C ₂ H ₆ , Plat. Pt	1N H ₂ SO ₄ 1N KOH	21-97	Q, θ as $f(T)$	A	67
C ₂ H ₄ , Pt	1N H ₂ SO ₄	30-70	θ as $f(T, V, \text{conc}, \text{time})$ energetics of ads.	I	12
C ₁ -C ₄ hydrocarbons } Plat. Pt	H ₂ SO ₄ , KOH KHCO ₃	25-65	Q , volume ads.	A,J	68
C ₂ H ₄ , C ₂ H ₂ , Pt	1N HClO ₄	30,60	Q as $f(V, \text{time})$	B,D	69
C ₂ H ₆ Pt	1N HClO ₄	60	Q as $f(V, \text{time})$	B,D	70
C ₂ H ₆ , C ₄ H ₁₀ , C ₈ H ₁₈ } Pt	1M H ₂ SO ₄	25,65	Q as $f(V, \text{time})$ θ as $f(V, \text{conc})$	A,I	71
C ₃ H ₈ , Pt	13M H ₃ PO ₄	80,110	Q as $f(V, \text{time})$	A,C	72
C ₂ H ₆ , Plat. Pt	4.3N HClO ₄	60	Q as $f(V, \text{time})$	B	73
C ₃ H ₈ Pt	80% H ₃ PO ₄	80-140	θ, Q as $f(V, T, \text{time})$	A,C	74
C ₄ H ₁₀ , Plat. Pt	3.7M H ₂ SO ₄	95	θ, Q as $f(V, \text{time})$	B	75
C ₄ H ₆ , Pt	NaC ₂ H ₃ O ₂	?	Capacity as $f(V, \text{conc})$	K	76
C ₆ H ₆ , Pt	H ₂ SO ₄ , H ₃ PO ₄ , NaOH	30-70	θ as $f(V, \text{conc}, \text{time}, \text{pH})$ energetics of ads	I	13
naphthalene Au benzene } naphthalene } Au phenanthrene } cyclohexane }	HClO ₄ , NaClO ₄	25	Γ, θ as $f(V, \text{conc})$	I	77
naphthalene } Ni, Fe, Cu, Pt	1N H ₂ SO ₄	25	θ as $f(V, \text{conc}, \text{time})$	I	78
naphthalene } Ni, Fe, Cu, Pt	1N NaClO ₄	25	Γ or $f(V, \text{conc})$ free energy	I	21
n-decylamine } Ni, Fe, Cu, Pb, Pt	NaClO ₄ , NaOH	25	Γ as $f(V, \text{conc})$ free energy	I	22
thiourea, Ni	0.5M Na ₂ SO ₄	25	Γ as $f(\text{conc})$	I	79
CH ₃ COONa	0.1N Na ₂ SO ₄	?	Γ , capacity as $f(V, \text{conc})$	E,I	80
CF ₃ COOH/CF ₃ COOK, } Pt, Au, Pd HCOOH/HCOOK, }	aqueous and nonaqueous	5-30	Q, θ , capacity	A,C,K	81
CH ₃ COOH/ } Pt, Au, Ir, Ni CH ₃ COONa }	buffers	20	Q	A	82

*A— anodic galvanostatic charging; B— linear anodic potential sweep; C— cathodic galvanostatic charging; D— linear cathodic potential sweep; E— ac impedance; F— differential capacitance from galvanostatic pulse; G— ellipsometry; H— uv absorption in solution; I— radiotracer; J— volumetric; and K— potential decay.

435 cm^{-1} , but no other. Introduction of oxygen into the system gave several other bands. From this he concluded that the two strong bands arise from independent structures but that there is no evidence to assume a bridged structure. Using field emission and ion microscopes, considerably more detailed information for the adsorption of CO on W has been obtained (86). Four distinct states of adsorbed CO were found with desorption energies of 20, 53, 75, and 100 kcal/mole. The α state (lowest desorption energy) was characterized by a spread of interaction energies, was formed on bare metal sites only in the presence of other states, and was in equilibrium with CO gas. The other three states, β_1 , β_2 , and β_3 , occurred on distinct crystal planes. The low-index planes, particularly the (110) plane, were covered only after the other planes were already heavily covered with CO. It was suggested that all the planes were involved in bonding the energetic β states, and therefore special planes on which only the α form might be held were unlikely. Ehrlich further suggested that the complexity of the surface system is such that generalizations are difficult and must be subjected to careful experimental tests. Another study, which applied spectrophotometric methods, proposed the presence of five different species of CO adsorbed on Ni (87) which were assigned to five observed intensity bands. The intensities of these adsorption bands were found to vary independently as the experimental conditions were changed (88), further suggesting that the species were different. Many of the observed variations may well be explained by the surface heterogeneity of the metal, which could have sites with a rather wide range of adsorption energies. Studies of metal surfaces now being made, for example, with low-energy electron diffraction show that the adsorption of a single gas on a single crystal surface is vastly more complex than had been previously imagined (7). Clean metal surfaces are not static assemblies of atoms; the surface atoms have a degree of mobility and when a gas is strongly adsorbed the substrate atoms can move to new positions. This surface reconstruction often occurs readily at room temperature and is well known, *e.g.*, for oxygen adsorption. Burwell and Peri (89) have concluded from their review of CO adsorption that more careful study is needed, and especially independent verification of band assignments which have been based on

doubtful analogies to spectra of simple carbonyls or gaseous CO ions. The same statement that more careful study is needed is even more true of CO electrosorption where the work has been very limited and the methods very few.

Formic Acid

The chemisorption of formic acid on Pt anodes has been studied only by coulometric methods. The information obtained from these measurements is summarized in Fig. 1. Typical "bell-shaped" behavior of the coverage-potential curves is observed for those cases which have been corrected for hydrogen coverage. The rate of adsorption of HCOOH was found to be fairly slow, 150 sec being required to obtain equilibrium coverage (35). It was concluded that formic acid is adsorbed according to a Langmuir-type isotherm.

The nature of the electrosorbed species has been the subject of much discussion, with the result that several possibilities have been proposed with no definite conclusion being formed. In the solution phase, evidence on the type of adsorbed species is necessarily indirect. The information, primarily obtained from the anodic oxidation of HCOOH, concerning the nature of adsorbed HCOOH is summarized in Table 8 (see Ref. 4). It would appear that the formic acid molecule is

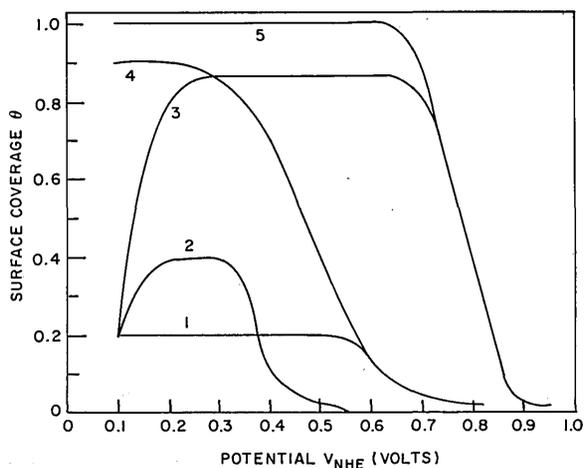


Fig. 1 — Fraction of Pt surface covered with HCOOH under various experimental conditions: (1) 10^{-4}M , 30°C ; (2) 1M , 90°C ; (3) 1M , 25°C ; (4) 1M , 40°C ; and (5) 1M , 30°C . (From Refs. 35-37.)

TABLE 8
Evidence for the Nature of Electrosorbed HCOOH

Species	Observation	Ref.
HCOOH	Optimum acidity for oxidation is in the range of pH 0-1	90
HCOOH	Addition of HCOOH caused no change in cyclic polarograms in 2N NaOH, while oxidn. peaks were observed in 2N H ₂ SO ₄	91
HCOOH	Observed c.d. for HCOOH oxidn. were much larger than could be accounted for by the calculated limiting diffusion currents of other species (HCOO ⁻ , (HCOOH·HCOO) ⁻ , (HCOOH) ₂ , etc.)	35
not HCOO ⁻	Methanol oxidized almost quantitatively to formate in basic soln., but completely to CO ₂ in acid.	41,90,92
not HCOO ⁻	θ decreases with increasing anodic potential, making adsorb. of a negatively charged species unlikely	36
not HCOO	Max. charge observed for adsorb. from anodic charging ($Q = 210 \mu\text{coul}/\text{cm}^2$) would imply area of formate radical of 7 \AA^2 as compared with $\sim 14 \text{ \AA}^2$ for HCOOH	36
not CO	Q for CO at $\theta = 1$ ($\sim 340 \mu\text{coul}/\text{cm}^2$) is higher than Q for HCOOH ($\sim 210 \mu\text{coul}/\text{cm}^2$) and anodic traces are significantly different	36
not CO	Lack of similarity in cyclic polarograms for oxidn. of CO and of HCOOH	93
not CO	CO requires much higher potential to oxidize than HCOOH	30,34

favored by the available evidence for electro-sorption. Considerably more work on this subject has been done in the gas phase in connection with the catalytic decomposition of HCOOH. This has recently been summarized by Bond (1) who concludes "It is evident that there remains substantial disagreement concerning the normal adsorbed state of formic acid. There is a *prima facie* case for believing that the structures and species present on nickel are not the same at all temperatures." The absorption bands observed with infrared have been generally assigned to the formate ion (HCOO⁻) by analogy with metal formates. It appears that the formate ion is formed on Ni catalysts between 20° and 100°C. The formic acid molecule is favored at -60°C. On MgO at temperatures below 100°C, the formic acid molecule has been favored (94). From mechanism studies of HCOOH decomposition over Al₂O₃ and MgO, the formate ion is formed at 200°C (95). From infrared spectra for HCOOH adsorption on Pt, the formate ion has been suggested as the

adsorbed species (96). On Ni it has been concluded that the adsorbed species was positively charged (97), negatively charged (1,98), or the covalently chemisorbed neutral molecule (99). Mars *et al.* (98) have suggested that differences in results may in part be due to observations on Ni-H catalysts rather than free Ni since at lower temperatures HCOOH cannot displace adsorbed H. They conclude that more surface coverage measurements are needed, particularly with special precautions taken to prevent poisoning or contamination, and that a lack of knowledge of the precise distribution of exposed crystallographic planes and the number of sites necessary for the adsorption of a single molecule must be filled in.

A survey of mechanism studies on the anodic oxidation of formic acid indicates that a process involving the dissociative adsorption of HCOOH is favored (4). Such studies have not been carried out in sufficient detail or under acceptable control of the system to permit reliable conclusions concerning the mechanism. The situation could be

considerably clarified by establishment of the nature of the species participating in the reaction, *i.e.*, the adsorption process.

Alcohols

Typical curves for the potential dependence of coverage obtained for the adsorption of methanol on Pt anodes determined by coulometric measurements are given in Fig. 2 (from Ref. 83). The potential and concentration dependence are very similar to that generally found for the electroadsorption of neutral organic molecules. It has been suggested that methanol adsorption follows the Temkin isotherm and that the potential at which the methanol coverage begins to decrease coincides with the potential of oxide formation (42). These points should receive further attention for experimental confirmation.

The principal gas-phase studies with alcohols bearing on the nature of adsorption concern catalytic dehydrogenation, which is the predominant process occurring when alcohols decompose on metal catalysts. In general, it has been found that primary alcohols yield aldehydes; however, methanol commonly decomposes to CO and H₂, and secondary alcohols yield ketones (1). Since dehydrogenation of alcohols is an endothermic process, it will be favored at increased temperatures. From an analysis of gases evolved when a platinized Pt electrode is immersed in solutions of alcohols, processes of dehydrogenation, hydrogenation, and self-hydrogenation were proposed (100). When the Pt electrode is saturated

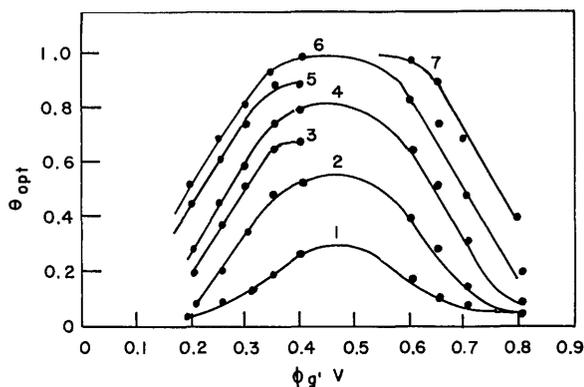
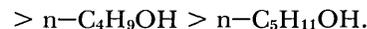


Fig. 2 — Dependence of methanol adsorption on the electrode potential in 1N H₂SO₄ and various methanol concentrations: (1) 10⁻³M; (2) 10⁻²M; (3) 5 × 10⁻²M; (4) 10⁻¹M; (5) 5 × 10⁻¹M; (6) 1M; and (7) 5M. (From Ref. 83.)

with hydrogen, the hydrocarbon containing the same number of carbon atoms as the original alcohol predominates in the gas phase. A Pt electrode essentially free from hydrogen gives predominately cleavage between the first carbon atoms. Decomposition of the C₁—C₂ bond proceeded more readily with aldehydes than with ethanol. It was concluded that alcohols in the presence of Pt electrodes are thermodynamically unstable substances. This point has been examined in more detail by studies of the open-circuit potential behavior by Podlovchenko (100) and will be discussed in a later section.

A few studies, particularly using infrared techniques, have been concerned with the structures of adsorbed alcohols. The interaction of ethanol with Al₂O₃ was reported to yield surface esters of the type Al—O—C₂H₅ (101). The only stable surface species produced by the adsorption of methanol on silica-supported Ni at 20°C was chemisorbed CO (102). The principal reaction of ethanol on Ni was to break the carbon-carbon bond, producing an adsorbed hydrocarbon fragment and chemisorbed CO. Some ethanol was also thought to produce a species of the structure CH₃—CH₂—Ni or CH₃—CH₂—O—Ni (102). Blyholder and Neff noted the ready cleavage of C—C and C—H bonds when one of the carbons had an attached OH group. The rapid exchange of the hydroxyl hydrogen with deuterium on metal catalysts suggested that the first step in alcohol decomposition is dehydrogenation to an aldehyde, which further decomposes with breakage of the C—C and C—H bonds. From a gravimetric study of alcohol adsorption on Al₂O₃ catalysts, the following conclusions were suggested (103):

1. The monolayer adsorption at 25°C of lower normal aliphatic alcohols on a number of Al₂O₃ catalysts decreases in the order



2. At moderate temperatures, besides orientations of alcohol molecules normal to the catalyst surface (adsorption due to hydroxyl groups), planar orientation also occurs (molecule adsorbed flat on surface).

3. At higher temperatures, the molecules of all alcohols are uniformly oriented with their

hydroxyl groups directed towards the catalyst surface.

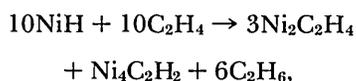
4. Adsorption from gas phase and from solution are not always comparable because the presence of adsorbed solvent molecules can affect the orientation of the alcohol molecules.

No mention of the various decomposition processes of alcohols was made in this study.

Hydrocarbons

The adsorption of hydrocarbons on transition metals has been extensively studied in the gas phase with a particular emphasis on whether adsorption is associative or dissociative. These studies are of particular interest in electrosorption where fairly detailed studies of ethylene have been made. We shall attempt to summarize the results of hydrocarbon adsorption measurements in the gas phase and then compare these with adsorption at electrodes in solution.*

The results of Twigg and Rideal (104) on the hydrogenation of C_2H_4 at Ni surfaces could be best explained if the carbon-carbon double bond broke in chemisorption, giving a complex bond by two-point attachment, *i.e.*, $NiCH_2-CH_2Ni$. Subsequent work by Conn and Twigg (105) and by Beek *et al.* (106), confirmed this conclusion. Twigg and Rideal (107) were able to show that favorable spacing of the metal atoms for this mechanism were available on Ni and the other metals active in catalyzing ethylene hydrogenation. However, using Ni films, Beek (108) found that the main process involved breakage of C-H rather than C-C bonds. Trapnell (109) concluded that initial chemisorption of C_2H_4 on W films was a four-site process but that final adsorption was a two-site process. He also found that hydrogen gas is evolved when C_2H_6 is adsorbed on several metals but that CH_4 was not extensively sorbed and no gas liberation was detected (110). This point was confirmed by Wright and co-workers (111). Jenkins and Rideal (112) obtained results from self hydrogenation of C_2H_4 on Ni which fit the equation



*The author wishes to acknowledge use of a summary of ethylene adsorption prepared by Mr. B. Rubin.

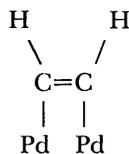
suggesting that associative and dissociative adsorption occur simultaneously. From the change in magnetic susceptibility of Ni powder during chemisorption of C_2H_4 at room temperature, Selwood (113) favored a two-bond adsorption. Assuming that the formation of a Ni-C bond affects the magnetic properties of Ni in the same way as a Ni-H bond, the chemisorption of C_2H_4 resulted in the Ni gaining, on the average, slightly more than two electrons per molecule. This implies that most of the ethylene is associatively sorbed but that a moderate fraction is held in a dissociated form requiring four or more sites. The C_2H_4 on Ir was found to undergo self-hydrogenation to C_2H_6 at both 27°C and 100°C, with some CH_4 also produced (114). The degree of self-hydrogenation of C_2H_4 and of decomposition of C_2H_6 was strongly dependent on the initial amounts adsorbed.

In a study of the adsorption of hydrogen and several hydrocarbons on Ir, using a field emission microscope, Arthur and Hansen (115) found that below 77°K H_2 , C_2H_2 , and C_2H_4 are chemisorbed and both C_2H_2 and C_2H_4 are adsorbed without dissociation. The hydrocarbon species once chemisorbed were substantially immobile below 700°K. Ethane was largely physically adsorbed and a large portion was readily desorbed at 100°K, although residues remained which were not desorbed below 1000°K. Above 200°K, C_2H_4 decomposed on Ir to C_2H_2 and H, the H being desorbed in the temperature range 250-400°K while the C_2H_2 dehydrogenated in the range 400-600°K to form a carbon residue. Bond (1) has concluded that self-hydrogenation is absent from ethylene chemisorption at -78°C on Ni films and is of little importance over Pd at this temperature, where most of the C_2H_4 is held by associative attachment in which the π bond is broken and two carbon-metal bonds are formed. There is also considerable evidence for the associative form existing after C_2H_4 sorption on H-covered Ni-silica and on films when the resulting complex is exposed to hydrogen.

Infrared studies of olefin adsorption indicate the presence of both olefinic and paraffinic C-H bonds (99,116). More recent magnetic susceptibility measurements by Selwood (117) favor associative adsorption of C_2H_4 on Ni at 0°C, but the dissociatively adsorbed species becomes more important at 28°C. Results of radiochemical

studies (118) of ethylene chemisorption on Ni, Rh, Pd, Ir, and Pt indicate two modes for adsorption, one being involved in hydrogenation and molecular exchange, the other being an inert form which is retained on the surface. These two modes were supposed to be associative and dissociative adsorption, and better correlation of results was obtained if the retained, *i.e.*, unreactive, species was considered to be associatively bonded. It was shown that acetylene could cause desorption of even the portion of the adsorbed ethylene layer which was retained in other experiments. Once adsorbed, the C_2H_2 behaved in a manner similar to C_2H_4 in the presence of hydrogen with regard to extent of retention on the surface. The retentions of C^{14} were further in agreement with observations that C_2H_4 adsorption on evaporated Ni, Pd, and W is accompanied by the production of C_2H_6 by self-hydrogenation. Fragmentation of the adsorbed species appears to become increasingly important as the temperature is increased. Other evidence for retention of the double bond in adsorption, *i.e.*, associative adsorption, is obtained from studies of olefin and acetylene complexes of transition metals (119). In olefin complexes of Ag and Pt, the olefin proton resonance (from proton resonance spectra) does not differ greatly from that in the free olefin, which is a good indication that the double bonds are retained (120).

The structure of chemisorbed acetylene has not been definitely resolved, although several studies determining the infrared spectra of the sorbed species on several metals have been carried out (121). The spectrum observed after chemisorption of C_2H_2 on a Pd-silica catalyst showed no evidence for C-H bonds of saturated hydrocarbons. Absorption bands at 3090 and 3030 cm^{-1} were attributed to C-H stretching vibrations of olefinic species (116). Eischens indicated that the preferred structure for adsorbed acetylene is of the form



A number of studies of the electrosorption of hydrocarbons, particularly ethylene, benzene, and

propane on Pt, have been carried out as indicated in Table 7. Typical results for the adsorption of ethylene on Pt as determined by the radiotracer technique are seen in Fig. 3 (12). A Langmuir-type adsorption isotherm was observed and the rate of ethylene adsorption was controlled by diffusion to the Pt surface. The mode of adsorption was considered to be associative. Calculations of the energetics of adsorption from gas-phase data show that the associative mode is only slightly favored over the dissociative mode. Such calculations are limited, however, since the bond energies in adsorbed species are not likely to be the same as in the gas phase. Further support for associative adsorption of C_2H_4 is obtained from a comparison of the kinetics of the anodic oxidation of C_2H_4 (122) and C_2H_2 (123). The 2.3 (RT/F) Tafel slope for C_2H_2 oxidation as compared with a 2.3 (2RT/F) Tafel slope for C_2H_4 indicates that the reactions have different rate-limiting steps. This suggests that the reacting species are different, which is not the case if C_2H_4 were dissociatively adsorbed.

The degree of surface coverage of Pt electrodes by C_2H_4 has been the subject of some discussion. The first coverage measurements reported for the adsorption of C_2H_4 on platinized gold foil electrodes from 1N NaOH at 60°C using the radiotracer technique found a low coverage on the order of $\theta = 0.1$ (65). Similar values of θ were reported for adsorption onto platinized Pt at 80°C from 1N H_2SO_4 using coulometric techniques (66). Refined measurements (12) with the radiotracer method for adsorption from 1N H_2SO_4 from 30-70°C onto platinized Au gave limiting coverages in the range $\theta = 0.35-0.4$. These coverage values were obtained assuming a double-layer capacity for the Pt electrode similar to that for Hg in order to calculate surface area. Volumetric and galvanostatic studies of C_2H_4 adsorption onto Pt black electrodes gave limiting coverages in the range of $\theta = 0.75-0.77$ (68). Further results using coulometric techniques found a limiting coverage for ethylene of $\theta = 0.75$ and also indicated that, on the average, 3.5 sites per C_2H_4 molecule were required for adsorption (69). These latter results are in agreement with results from steady-state kinetic measurements which required high coverage, in the range $\theta \geq 0.8$ and about four sites/molecule, to correlate the experimental data with the proposed mechanism (122). The

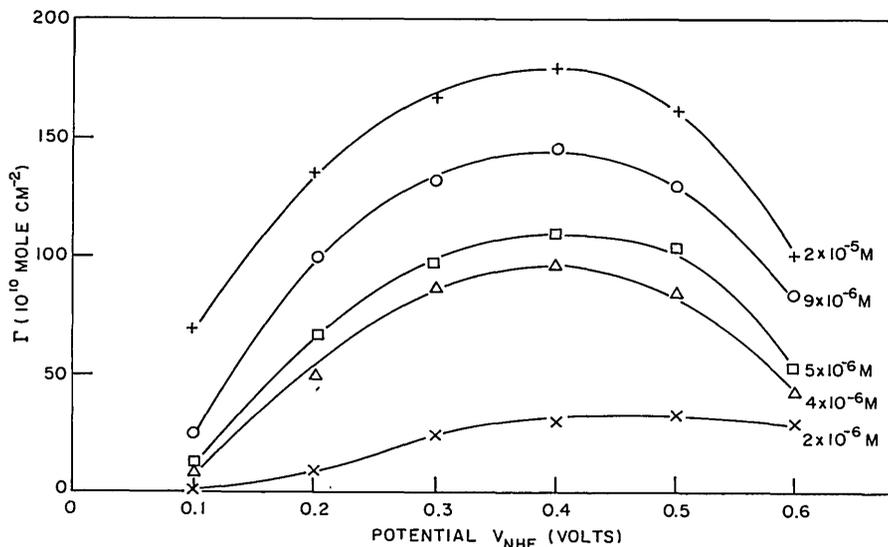


Fig. 3 — Ethylene coverage as a function of potential on a platinum electrode in 1N H_2SO_4 : (+) $2 \times 10^{-5} M$, (O) $9 \times 10^{-6} M$, (□) $5 \times 10^{-6} M$, (Δ) $4 \times 10^{-6} M$, and (×) $2 \times 10^{-6} M$. (From Ref. 12.)

differences between the radiotracer measurements and the coulometric results probably lie primarily in the surface area determinations, a factor of two being easily explicable. The fact that C_2H_4 appears to be adsorbed associatively on electrodes, while both associative and dissociative adsorption may occur in the gas phase, is again attributed to the presence of water molecules on the electrode surface.

The adsorption of several saturated hydrocarbons onto Pt black electrodes has been examined by volumetric and galvanostatic methods (68). The results showed that hydrocarbons fall into several groups in terms of surface coverage. Methane is adsorbed to only a small extent, *i.e.*, $\theta < 0.1$. Higher-molecular-weight saturated hydrocarbons adsorb to a somewhat greater extent, *e.g.*, C_2H_6 and C_3H_8 give $\theta \approx 0.2-0.3$. Unsaturated hydrocarbons give θ on the order of 0.7-0.8. These results are essentially in line with gas-phase studies which show that saturated hydrocarbons are often only physically adsorbed. The electrolyte from which adsorption was carried out had a marked effect on the adsorption behavior of saturated hydrocarbons. However, no detectable effects were observed for unsaturated compounds. This may be understood in view of the necessary replacement of adsorbed species, which would depend on the electrolyte, and the energetics of

dissociative adsorption. Further studies of ethane electroadsorption have indicated that the structure of the adsorbed species consists of species between the composition of C_2H_2 radical and CO (73). From galvanostatic studies of propane adsorption on Pt it was suggested that at 0.2 V_{NHE} each C_3H_8 molecule covered one Pt surface atom, but at from 0.3-0.5 V three sites were involved (72). At 0.25 V the initial chemisorption appeared to be on one site, but then reverted to three-site attachment, and all subsequently chemisorbed material occupied three sites. Propane was assumed to dissociate on the Pt surface. Studies to elucidate the structure of the adsorbed propane species using anodic desorption techniques suggested that three distinct adsorbed residues were present (74). These were supposed to release 1.8, 1.3, and 6 electrons per covered Pt site when oxidized. Studies of butane adsorption on Pt black gave indications of some fragmentation of the hydrocarbon on the surface (75). The adsorption of butane has been indicated to be diffusion controlled from radiotracer measurements (71). However, coulometric methods have suggested that adsorption, rather than mass transport, was the limiting factor (75). In general, the assignment of structure to adsorbed species from the various coulometric methods has been by indirect and, in general, rather obscure methods. Thus, it would

seem that conclusions from these types of measurements should be taken with considerable caution. In general, it should be expected that saturated hydrocarbons would undergo dissociation and possibly fragmentation in adsorption since there is no other way to chemisorb.

The rate of benzene adsorption (13) was found to be controlled by mass transfer at low coverages, as indeed was the electrosorption of most hydrocarbons studied. Benzene was found, however, not to fit either a simple or modified Langmuir adsorption isotherm, but fairly good agreement with the Temkin isotherm was obtained (13). It was suggested that benzene adsorbs on Pt with a probable loss of aromatic character, *i.e.*, by breaking the double bonds, and that on the average nine water molecules were replaced by a single benzene molecule. Radiotracer studies of the electrosorption of several aromatic hydrocarbons at the Au-electrolyte interface have shown that the planar, *i.e.*, flat, orientation of the adsorbed species is preferred (78). Naphthalene adsorbs parallel to the electrode surface on several metals and there are indications that some π -bonding may occur (21). In the adsorption of *n*-decylamine, best agreement with experiment was obtained by assuming nonlocalized adsorption and nonrigid molecules allowing the formation of dipole pairs (21). The orientation of the adsorbed species was found to depend on the metal electrodes, *e.g.*, the amine group was adsorbed towards the metal on Pt but towards the solution on Cu and Ni.

In general, one finds that where comparable systems have been studied, agreement between gas-phase adsorption and electrosorption is found. There is a need for considerable experimental work before valid structure can be assigned to adsorb species both in the gas phase and at electrodes in solution. It should be noted that the tendency to dissociate and fragment in gas-phase adsorption is considerably lessened in electrosorption, probably due to the presence of solvent molecules on the electrode surface. This point shall now receive further attention in reference particularly to alcohols which have been examined by Frumkin's school using open-circuit potential measurements.

OPEN-CIRCUIT ADSORPTION BEHAVIOR

The subject to be discussed here is not the mechanism of establishment of open-circuit

potentials in the presence of organic species, which has already been reviewed to some extent (4), but the information which such studies have given concerning the nature of the adsorption process and the adsorbed species. Mass-spectrophotometric analysis of gases produced when acetaldehyde was added to a 0.1N H₂SO₄ solution at a platinized Pt electrode gave 46% C₂H₆ and 54% CH₄, indicating hydrogenation (124), when the electrode potential was negative to 0.080 V_{NHE}; at higher electrode potentials, acetaldehyde was assumed to dehydrogenate. Halide ions retarded both the dehydrogenation and hydrogenation processes. Propanol and butanol were assumed to be hydrogenated when added to a platinized Pt electrode at 0.060 V (124). Analysis of the gaseous products gave for propanol, 75% C₃H₈, C₂H₆, and small amounts of C₂H₄, and for butanol, 76% C₄H₁₀, 23% C₃H₈, C₂H₆, C₂H₄, and 1% CH₄. These results were found in disagreement with reported liquid-phase catalytic studies which reported no hydrogenation of C₃H₇OH or C₄H₉OH at platinized Pt. It was concluded that the C—O bond undergoes hydrogenation to the greatest extent, the C₁—C₂ bond to a much smaller extent, and there is practically no cleavage of the other C—C bonds. For the hydrogenation process to occur it was considered essential for the alcohol molecule to be oriented either with the OH group toward the metal surface or, more probably, for the molecule to be adsorbed flat on the surface. The slight maximum before the beginning of the potential plateau for galvanostatic charging curves of acetaldehyde adsorbed at a Pt electrode from 0.1N H₂SO₄ were explained by polymerization of the CH₃CHO which required additional energy for oxidation to begin (125).

Podlovchenko and Gorgonova suggested that their experimental data on methanol adsorption on Pt obtained from charging curves was in good agreement with the hypothesis that dehydrogenation products of CH₃OH are chemisorbed on the platinized Pt surface (45). It was also suggested that possibly a stronger chemisorption is characteristic of species containing oxygen. From a detailed analysis of the data it was supposed that methanol molecules primarily yield three hydrogen atoms on adsorption and a particle of the type

$$\begin{array}{c} \text{O}-\text{C}-\text{H} \\ | \quad || \end{array}$$

was left chemisorbed on the Pt. In this treatment it was assumed that the chemisorbed

species occupied just as many sites as it gives up electrons upon oxidation. These authors also stated that in spite of the possibility of obtaining specific information with the anode pulse method, *e.g.*, as used by Breiter and Gilman, it cannot be stated with complete assurance that their adsorption measurements pertain to adsorbed CH_3OH and do not include to a significant degree the chemisorbed products of its oxidation.

The introduction of propyl alcohol to a platinized Pt electrode at 0.064 V_{NHE} resulted in the evolution of gases which consisted of 19% C_2H_6 , 76% C_3H_8 , and 4% C_4H_{10} (126). Gases evolved at platinized Pt at 0.041 V consisted of <1% CH_4 , <1% C_2H_6 , 23% C_3H_8 , and 76% C_4H_{10} , while at 0.50 V an analysis of the gases gave 2% C_2H_6 , 69% C_3H_8 , and 28% C_4H_{10} . The final products were strongly dependent on the potential at which the alcohol was introduced into the system. It was observed that dehydrogenated species could have rather large effects on electrode processes. For example, the formation of residues poisons the electrode and prevents the oxidation of alcohols; at 0.40 V, the rate of oxidation of alcohols decreased by a factor of 10^4 from processes occurring on clean electrodes. By adsorbing molecules, removing the electrode and washing it, and then oxidizing the material remaining on the electrode, the nature of the adsorbed species was examined. Tafel lines obtained in methanol solution were compared with Tafel lines obtained by oxidizing the residue remaining after electrode washing, and a difference in overvoltage of only about 40 mV was found (126). From this it was concluded that the oxidation of methanol was limited by the rate of removal of the firmly bound species. Larger overvoltage differences were found with other alcohols and with HCOOH , the difference being such that it could not be assumed that the firmly bound residue was an intermediate.

When alcohols were brought in contact with a degassed platinized Pt electrode, a cleavage of the $\text{C}_1\text{--C}_2$ bonds was predominant (100). A decomposition of the $\text{C}_1\text{--C}_2$ bond was found to proceed considerably more readily for acetaldehyde than for ethanol. This parallels a suggestion from gas-phase studies (102) that aldehydes are more easily decomposed than alcohols. For ethanol, only about half of the chemisorbed species could be displaced by interaction with hydrogen. The

amounts of chemisorbed ethanol and hydrogen were strongly dependent on the ethanol concentration. However, the final values of the open-circuit potentials were essentially independent of concentration and were assumed to be determined by hydrogen. For a number of substances, the final value of the open-circuit potential was independent of the potential at which the substance was introduced into the system; however, aldehydes were an exception to this. It was proposed that the steady states of the surface for several substances differ considerably when they are introduced at low and high values of potential, *e.g.*, as a result of chemisorption of various oxidation products.

The behavior of methanol at Pt electrodes differed considerably from that of other saturated alcohols, presumably due to the absence of the C--C group (46). At low potentials, near zero on the hydrogen scale, no gas was evolved from methanol adsorption, and chemisorbed species did not accumulate with time.

In summary, it appears that when a steady potential is established at platinized Pt electrodes in solutions of alcohols and aldehydes containing more than one carbon atom, processes of dehydrogenation and self-hydrogenation of the original substances and their decomposition products (mainly along the $\text{C}_1\text{--C}_2$ bond) occur (55). A steady concentration of H_{ads} on the electrode surface, established and maintained by these processes, determines the final open-circuit potential.

Several suggestions concerning the nature of the species resulting from methanol and formic acid have been made and discussed. Many investigators have accepted a proposal by Giner (127) of a "reduced CO_2 " species having the form of carbon monoxide or formate radical. Investigation by Vielstich (93) have shown conclusively that the species resulting from HCOOH adsorption is not CO . More recent investigations of the nature of the interaction of CO_2 with adsorbed H have shown that the assumption of CO_2 reduction is not necessary and that the results could be better explained by a simple poisoning of the H oxidation by interaction with CO_2 (128). It may be suggested that this type of process, *i.e.*, interaction of CO_2 resulting from oxidation of the organic with hydrogen present on the electrode, may be a general poisoning species below 0.3 V_{NHE} .

SUMMARY

In the past, electrosorption studies have contributed little to the general knowledge of adsorption phenomena and have relied heavily on gas-phase studies. While there are many techniques available for the study of gas-phase adsorption that cannot be used when solvent is present, they have not been used with great success to determine the nature of adsorbed species at the electrode surface. It would be of great value to have more detailed studies of systems in the gas phase, which could then be compared with solution-phase adsorption at electrodes. The addition of water vapor in gas-phase studies would greatly aid in making comparison with solution-phase measurements since then both processes would be competitive or replacement reactions. The presence of solvent molecules is the one large difference in electrosorption measurements, and this is strongly in evidence in the energetic aspects of adsorption. The ability to vary the energy of the systems much more readily at electrodes, *i.e.*, by control of the metal-solution potential difference, is a considerable advantage for electrosorption.

In general, it can be stated that the surface structure of adsorbed organic species has not been established for any case in electrosorption, but this structure also has not been established for any case in the gas phase. Considerable progress has been made in gas-phase study by the introduction of ultrahigh vacuum techniques, with a strong emphasis on system purity and control. While such techniques are not applicable to electrosorption, the control of system and purity are extremely important, and improved techniques and procedures are now becoming available. Finally, it should be stated that gas-phase catalysis and electrosorption are not unrelated since both are aspects of adsorption and each will have much to contribute to the other if high standards of quality in experimental measurement are required and maintained.

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13. ABSTRACT <p>A review of the methods used to investigate the adsorption of organic compounds on solid metal electrodes shows that all of the available methods have very definite limitations. In the absence of a really good method, it is wise to employ all the available techniques which give complementary information.</p> <p>The available experimental information obtained from electrosorption measurements is compared with the data obtained from gas-phase studies. As an example of the difficulty encountered in making a comparison of gas-phase and electrosorption measurements, it is found in the study of adsorption energetics that the heats of adsorption are much lower in electrosorption. When water vapor is present, electrosorption is most likely similar to competitive gas-phase adsorption. A discussion of the energetics of adsorption clearly shows the competitive nature of adsorption at electrodes in solution.</p> <p>The adsorption characteristics of carbon monoxide, formic acid, methanol, ethanol, and hydrocarbons, especially ethylene, are discussed in some detail.</p> <p>A review of adsorption phenomena observed at open circuit shows that when a steady potential is established at platinized Pt electrodes in solutions of alcohols and aldehydes containing more than one carbon atom, processes of dehydrogenation and self-hydrogenation of the original substances and their decomposition products occur.</p>			

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