Influence of Dipole Interactions on Surface Reactions

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Electrostatic interactions between dipoles of adsorbed molecules can influence reaction mechanism and kinetics. Repulsive interactions can increase the rate of surface reactions, whereas attractive interactions can decrease the rate of reaction because of an increased stability of the adsorbed species. With formic acid decomposition on Ni surfaces attractive dipole interactions resulted in the formation of a condensed surface phase, which decomposed with autocatalytic kinetics. The formation of the condensed phase was affected by both crystallographic structure as well as adsorption temperature by affecting the approach to an equilibrium configuration.

Attractive dipole interactions also affect the orientation of molecules on a surface, thus facilitating reactions that might not otherwise occur. The formation of methyl formate from formaldehyde on a $W(100)-(5 \times 1)C$ surface has been attributed to the favourable alignment of formaldehyde molecules stemming from attractive dipole interactions.

Adsorbate-adsorbate (A-A) interactions affect the adsorption/desorption behaviour of gases on metal surfaces. LEED studies have shown that ordered phases are formed due to these interactions.¹ Large changes in the isosteric heats of adsorption result from repulsive interactions between adsorbates.^{2, 3} In temperature programmed desorption experiments A-A interactions result in multiple desorption peaks. The effects of these interactions can be treated by statistical mechanics and models have been developed to explain temperature programmed desorption results in terms of adsorbate-adsorbate interactions.⁴⁻⁶

Most models have assumed the adsorbate interactions to be the result of indirect interactions through the metal surface. Theoretical evidence for oscillatory indirect A-A interactions *via* the substrate was first presented by Grimley.⁷ More recently Einstein and Schrieffer ⁸ have shown that the periodicity of this oscillatory behaviour is related to the periodicity of the substrate. These models have been useful in providing a basis for the existence of A-A interactions, correlating well with the observations for many ordered LEED patterns.

Over forty years ago both Langmuir and Roberts examined some implications of A-A interactions which they attributed to dipole-dipole interactions.⁹⁻¹¹ Most modern investigators have dismissed the importance of these dipole interactions; however, recent studies of adsorption and reactions of organic molecules on single crystal metal surfaces indicate that dipole interactions are important in determining reaction kinetics and in affecting reaction mechanisms. This paper discusses the nature of dipole-dipole interactions and how these interactions affected adsorption, surface reactions and reaction kinetics.

DIPOLE-DIPOLE INTERACTIONS

In order to have dipole-dipole interactions an adsorbed species must possess either a permanent dipole (e.g., the dipole of formaldehyde) or a dipole due to

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adsorption (e.g., oxygen adsorption on a metal will result in a polar M—O bond). The adsorption of two such molecules can be represented as in fig. 1. The total adsorption energy for these two molecules can be written as

$$E_{\text{total}} = E_0 + E_{\text{config}} \tag{1}$$

where E_{total} is the total adsorption energy, E_0 is the adsorption energy for isolated molecules and E_{config} is the configurational energy due to adsorbate-adsorbate interactions. The configurational term will include contributions both from the indirect interactions and the direct dipole-dipole interactions; only the latter will be considered in the following discussion.



FIG. 1.--Dipole orientation for adsorbed species.

The interaction energy between two dipoles with dipole moments μ_1 and μ_2 at large separation is given by classical electrostatics as

$$U = -\frac{\mu_1 \mu_2}{r^3} [2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2)]$$
(2)

where r is the distance between dipoles and the angles are as indicated in fig. 1. If it is assumed that the point dipole approximation is valid and that both adsorbed molecules are in the same configuration then the above expression reduces to

$$U = -\frac{\mu^2}{r^3} (3\cos^2\theta - 1).$$
 (3)

The significance of eqn (3) is that it shows that the molecular orientation affects the configuration energy. If the dipoles were aligned normal to the surface the configuration would be repulsive; whereas, if the dipoles lay in the plane of the surface the configuration would be attractive. The important feature to note is that if the dipole has a significant component in the plane of the surface it can lead to attractive interactions between adsorbates.

The net effect of dipole-dipole interactions can be either attractive or repulsive, depending on the orientation with the surface. Both attractive or repulsive interactions will result in the binding energy being dependent on the adsorbate coverage; however, the sign of the interaction will produce profoundly different effects in the adsorption process. At low coverage, repulsive interactions will result in adsorption being approximately spatially random as that will minimize the effect of the repulsive forces. Attractive interactions, on the other hand, will result in the adsorbed molecules condensing into islands where the binding energy is enhanced compared with random adsorption. For a given attractive interaction potential (ω) there will be a critical temperature (T_e) defined by

$$T_{c} = \frac{\omega}{2R} \tag{4}$$

below which a condensed phase will exist in equilibrium with a diffuse phase on the surface.¹² Above the critical temperature a single diffuse phase will exist, with approximately random distribution.

The effects of A-A interactions can best be seen in temperature programmed desorption experiments. Several previous investigators have treated the effects of repulsive A-A interactions on temperature programmed desorption using a quasichemical approximation. Adams⁴ has derived the following expression for the rate of desorption from a square lattice when only nearest neighbour interactions are considered

$$-\frac{d\theta}{dt} = \left(\frac{kT}{h}\right)\theta \left[\frac{1+\varepsilon}{1+\eta\varepsilon}\right]^4 \exp\left(-E_0/RT\right)$$

$$\eta = \exp\left(-\omega/RT\right)$$

$$\varepsilon = \{(2\theta-1) + [1-4\theta(1-\theta)(1-\eta)]^{\frac{1}{2}}\}/2\eta(1-\theta)$$
(5)

where θ is the fractional coverage, E_0 is the adsorption energy of an isolated molecule and ω is the interaction energy. This expression is also applicable for attractive interactions when the temperature is above the critical temperature, where random distribution is a reasonable approximation. Below the critical temperature, desorption can be described as occurring from two phases, a condensed phase where the rate of desorption should be pseudo first-order and a diffuse phase where the rate of desorption is described as above. Desorption from the condensed phase can also be described by the above expression, but using a local fractional coverage which is unity in the condensed phase.

Fig. 2 shows the desorption spectra as a function of adsorbate coverage for the three cases of (a) no interactions, (b) attractive interactions and (c) repulsive interactions. For all three cases E_0 was 102 kJ mol⁻¹, the pre-exponential factor was 1×10^{13} s⁻¹ and the heating rate (β) was 10 K s⁻¹. An attractive potential of 2.6 kJ mol⁻¹ and a repulsive potential of 4.2 kJ mol⁻¹ were chosen as typical values of dipole interactions in next nearest neighbour positions to generate the spectra shown in fig. 2(b) and (c). (These values were obtained from assuming a dipole moment of 1.7 D separated by 5 Å. The orientations were $\theta = 90^{\circ}$ for the repulsive configuration and $\theta = 30^{\circ}$ for the attractive configuration.) The three cases can be seen to give quite distinctive desorption behaviour as a function of adsorbate coverage. In the absence of any interactions the desorption peak temperature shows no variation This was first pointed out by Redhead¹³ and is the distinguishing with coverage. feature of a simple first-order reaction process. Atttractive interactions result in the adsorbate being more stable on the surface than if no interactions were present. The enhanced stability causes the desorption peak to shift to higher temperature with increasing coverage, as shown in fig. 2(b). This distinguishing feature of attractive interactions has only been reported for polar molecules like formaldehyde, or formic acid,^{14, 15} which has suggested the importance of dipole-dipole interactions. Repulsive interactions have been discussed previously with respect to through surface interactions.⁴⁻⁶ The desorption spectra in fig. 2(c) show that the binding energy decreased with increased coverage, due to repulsive interactions causing desorption at lower temperatures than if no interactions occurred. In particular one observes a low temperature desorption peak above a fractional coverage of $\theta = \frac{1}{2}$, as increasing adsorption above this point results in adsorbates being in nearest neighbour positions where the repulsive interactions are most significant. As will be discussed below both attractive and repulsive interactions have been observed experimentally and can be explained as the result of dipole-dipole interactions.



temperature/K



FIG. 2.—Temperature programmed desorption as a function of coverage for (a) $\theta = 1.0$, (b) $\theta = 0.75$, (c) $\theta = 0.50$, (d) $\theta = 0.25$. (A) First-order desorption. (B) First-order desorption with attractive interactions $\omega = 2.6$ kJ mol⁻¹. (C) First-order desorption with repulsive interactions $\omega = 4.2$ kJ mol⁻¹.

EXPERIMENTAL EVIDENCE FOR DIPOLE-DIPOLE INTERACTIONS

FORMIC ACID ON Ni(110) AND Ni(100)

Attractive dipole-dipole interactions for adsorbed species were shown by Benziger and Madix to have affected the kinetics of the decomposition of formic acid on Ni surfaces.¹⁵ Formic acid decomposed on Ni(110) and Ni(100) via the dehydration of two formic acid molecules to give a formic anhydride intermediate which subsequently decomposed by an autocatalytic process to yield H₂, CO₂ and CO.^{15, 16} Formic anhydride is a highly polar molecule and should display effects of dipoledipole interactions. Benziger and Madix proposed that the dipoles are tilted at an angle of 37° to the surface such that there is an attractive interaction between the adsorbed intermediates, which explained the unusual kinetics observed. The calculated attractive interaction potential was 11 kJ mol⁻¹ when all pairwise interactions were accounted for. The temperature for decomposition of the anhydride was well below the critical temperature ($T_c = 660$ K) so that one would predict that a condensed phase would form as the coverage increased. Condensation was clearly demonstrated by the work of Ying¹⁷ shown in fig. 3. At low coverages CO₂ was formed by the decomposition of the formic anhydride in the diffuse phase at 75° C. As the coverage was increased a condensed phase was formed, resulting in greater stability of the formic anhydride intermediate, which thus decomposed at a higher The emergence of the high temperature peak was the indication of temperature. condensation.

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The formation of a condensed phase on the surface was further exemplified by the work of Falconer and Madix.¹⁸ Deuterated formic anhydride (derived from DCOOH) decomposed at a higher temperature than normal formic anhydride. When DCOOH was first adsorbed on Ni(110) followed by adsorption of HCOOH two desorption peaks were observed for the CO₂ product, one coincident with D₂ desorption where the deuterated intermediate normally decomposed and the other coincident with H₂ desorption where normal formic anhydride decomposed. In



FIG. 3.—CO₂ desorption from formic acid decomposition as a function of coverage.¹⁷

contrast to this behaviour was that for coadsorption of DCOOH and HCOOH, where a single CO_2 desorption peak was found coincident with H_2 , D_2 and HD at a temperature intermediate to those normally observed for HCOOH and DCOOH adsorption. These results clearly showed the formation of a condensed phase; consistent with the model for attractive dipole interactions proposed by Benziger and Madix.

One unique feature of these attractive interactions was the autocatalytic reaction kinetics. As desorption occurred the binding energy of the remaining adsorbates decreased as the configurational interaction decreased. This led to an acceleration of the rate with decreasing surface concentration, or in other words an autocatalytic process. Such autocatalytic behaviour was observed by Falconer *et al.*¹⁹ where the

rate of reaction was observed to increase with decreasing coverage at constant temperature.

To complete the discussion of formic acid decomposition on Ni the effect of crystallographic structure on the dipole alignment should be mentioned. The Ni(110) and Ni(100) surfaces are shown schematically in fig. 4. Ying and Madix ²⁰ have shown that a four Ni atom cluster stabilized the formic anhydride on Ni(110) and proposed that the molecule was oriented such that the dipoles were aligned along the $(1\overline{10})$ direction. As the (110) surface is anisotropic there was a preferred orientation for adsorption of the formic anhydride so that island condensation was readily effected. On the other hand, the (100) surface is isotropic so that no preferred orientation for adsorption was indicated. The saturation coverage of the anhydride on Ni(100) suggested that a six Ni atom cluster was required for adsorption of the anhydride. Initial adsorption in the diffuse phase on the Ni(100) surface would result in the orientation of the molecules being random, inhibiting the subsequent alignment of the dipoles at higher coverages as shown in fig. 4 and hence reducing the overall attractive interaction in the condensed phase. This was observed by Benziger and Madix where the attractive interactions for Ni(100) were reduced by 50 % from those observed on Ni(110).15

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FIG. 4.—Formic anhydride island structure on Ni surfaces. (A) Ni(110), (B) Ni(100). ●, Nickel atom; ↑, formic anhydride.

METHANOL ON Ag(110)

The oxidation of methanol to formaldehyde on an Ag(110) surface with adsorbed oxygen was studied by Wachs and Madix.²¹ They observed that the adsorption of methanol was induced by the presence of preadsorbed oxygen. Employing isotopically labelled ¹⁸O₂ and CH₃OD they were able to show that each adsorbed oxygen atom induced the adsorption of two methanol molecules which subsequently formed methoxy intermediates as shown in fig. 5. This figure shows that the methoxy intermediates were formed in pairs so that a pairwise dipole interaction was expected. The tetrahedral coordination of the carbon in the methoxy group forces the dipole to be nearly normal to the surface so as to avoid repulsive interactions between the methoy intermediates. The repulsive dipole interaction should then result in the decomposition of the methoxy pairs by two sequential processes. In the first step the rate is

enhanced by the repulsive forces which reduce the stability of the methoxy intermediate. After the first methoxy has decomposed the second gains added stability because the repulsive dipole force has been eliminated and so the rate of decomposition is slower. The rate expression would be

$$\frac{\mathrm{d}\sigma}{\mathrm{d}t} = v(\sigma_1 + \sigma_2) \exp\left(-E_{\mathrm{a}}/RT\right) + v\sigma_2 \exp\left[-(E_{\mathrm{a}} - \omega)/RT\right] \tag{6}$$

where σ_1 is the coverage of the isolated methoxy, σ_2 is the coverage of the methoxy pairs and ω is the repulsive interaction energy. In a temperature programmed desorption experiment the dipole forces would result in two desorption peaks.



FIG. 5.—Mechanism for methanol oxidation on Ag(110).

Furthermore, if repulsive dipole forces were important then one would expect the adsorbed oxygen sequentially to induce adsorption of one molecule, then another, resulting in the high temperature desorption peak growing to saturation followed by the emergence of the low temperature peak. This behaviour, which is shown schematically in fig. 6 for $v = 10^{13} \text{ s}^{-1}$, $E_a = 105 \text{ kJ mol}^{-1}$ and $\omega = 10 \text{ kJ mol}^{-1}$, is identical to the observations of Wachs and Madix for formaldehyde formation from methanol on Ag(110). The repulsive interaction of 10 kJ mol⁻¹ was derived

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by assuming a dipole moment of 1.7 D for the methoxy supposing it to be oriented normal to the surface and a separation of 4 Å, which are typical values for methanol adsorbed at next nearest neighbour sties on the Ag(110) surface.²²



FIG. 6.-Effect of pairwise repulsive dipoles on temperature programmed desorption.

The repulsive interactions between methoxys were observed for low surface coverages (< 20 % of saturation coverage), indicating that the adsorbed intermediates remained adsorbed in adjacent positions and did not establish an equilibrium configuration during the time period of the experiment. Establishment of equilibrium is dependent on the rate of diffusion across the surface. Diffusion is temperature dependent so that the adsorption temperature will affect the approach to equilibrium and hence the interactions between adsorbates. This effect was also observed for formic acid decomposition on Ni(110) where decreasing the adsorption temperature of formic acid from 310 to 210 K resulted in an increase in the rate of decomposition of the formic anhydride and suppression of the formic anhydride to form a condensed phase, resulting in the increased reaction rate which occurred from the diffuse phase.

FORMALDEHYDE ON $W(100) - (5 \times 1)C$

The two previous examples have shown the effects of dipole-dipole interactions on the reaction kinetics. As a last example we consider a case where attractive dipole interactions influence the reaction mechanism. The adsorption of formaldehyde on a $W(100) - (5 \times 1)C$ surface resulted in a complex reaction scheme in which various hydrocarbons as well as CO and H₂ were formed.¹⁴ The initial reaction step was the decomposition of formaldehyde to CO and hydrogen, with much of the hydrogen reacting with adsorbed formaldehyde to form intermediates which led to hydrocarbon formation. The product desorption spectra were studied as a function of formaldehyde exposure and showed the CO and H₂ peaks, corresponding to the initial decomposition step, shifted to higher temperature with increasing formaldehyde

exposure, similar to the effect seen in fig. 2 for attractive interactions. Furthermore, as the coverage was increased above some critical coverage methyl formate was observed to desorb at low temperature by a desorption limited process (*i.e.*, methyl formate desorbed at the same temperature as when methyl formate was adsorbed), below the temperature at which formaldehyde decomposed.



FIG. 7.-Mechanism of methyl formate formation from formaldehyde.

The coverage dependence of formaldehyde decomposition indicated that attractive interactions were important, so the alignment of the dipoles of two formaldehyde molecules was considered. Fig. 7 shows the alignment of formaldehyde molecules on a surface due to attractive dipole-dipole interactions. As shown in fig. 7 this orientation is favourable for a hydrogen transfer leading to the formation of methyl formate. Attractive dipole interactions can thus influence the configuration of adsorbed species facilitating reactions which might otherwise not occur.

CONCLUSIONS

A simple approach to the interactions between the dipoles of adsorbed molecules has been presented. In reviewing the experimental results for reactions of simple organic molecules on metal surfaces the importance of these dipole-dipole interactions has been clearly demonstrated. The dipole interactions affect the orientation of adsorbed molecules as well as the adsorption energy. The distances over which these dipole interactions are of importance are much greater than the indirect interactions discussed by Einstein and Schrieffer, so that for polar molecules the through space dipole interactions would be expected to dominate. Furthermore, the dipole interactions can be strongly attractive, resulting in the formation of condensed surface phases, as seen in the case of formic acid decomposition of Ni(110).

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