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LINEAR FREE ENERGY RELATIONSHIPS FOR C_1-OXYGENATE DECOMPOSITION ON TRANSITION METAL SURFACES

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Linear free energy relationships for the decomposition of formate and methoxide intermediates on metal surfaces have been developed. These demonstrate that Group VIII and Group IB metals do not obey the same correlations. Implications of these observations include the potential for misinterpretation of classical Balandin "volcano" plots.

Keywords: Transition metal catalysts, formic acid, methanol, linear free energy relationships

The decomposition of formic acid has long been a common test reaction for examining the activity of metal catalysts. The variation of the activity of transition metals for this reaction forms the basis for perhaps the best known example of a "Balandin volcano curve" illustrating Sabatier's principle of the optimum instability of catalytic intermediates [1]. This reaction proceeds via a surface formate intermediate; these species are ubiquitous in studies of formic acid adsorption on metal single crystals. Platinum is the most active metal for formic acid decomposition; on metals where the enthalpy of formation of the formate is more negative, the formate is more stable and the steady state rate is lower; on Ag and Au decomposition is slower due to less favorable thermodynamics and kinetics of formate formation. If one considers *only* the thermal stability of formates, e.g., as represented by peak temperatures in TPD experiments, one would expect to observe only one "leg"of the volcano; i.e., the influence of the rate limiting formation of formates on the noble metals would be removed. Madix [2,3] has suggested, however, that the rate of formate decomposition alone appears to exhibit "volcano" behavior; i.e., the apparent activation energy for formate decomposition passes through a minimum value as one examines metals with increasingly negative enthalpies of formation of the formate (see fig. 1). As depicted, this clearly does *not* represent a *linear* free energy relationship of the sort implicit in Sabatier's principle or in the classical explanation of the Balandin volcano curve. Madix [3] has suggested that formate species are more stable on the IB metals than on the platinum group, in spite of less favorable thermody-

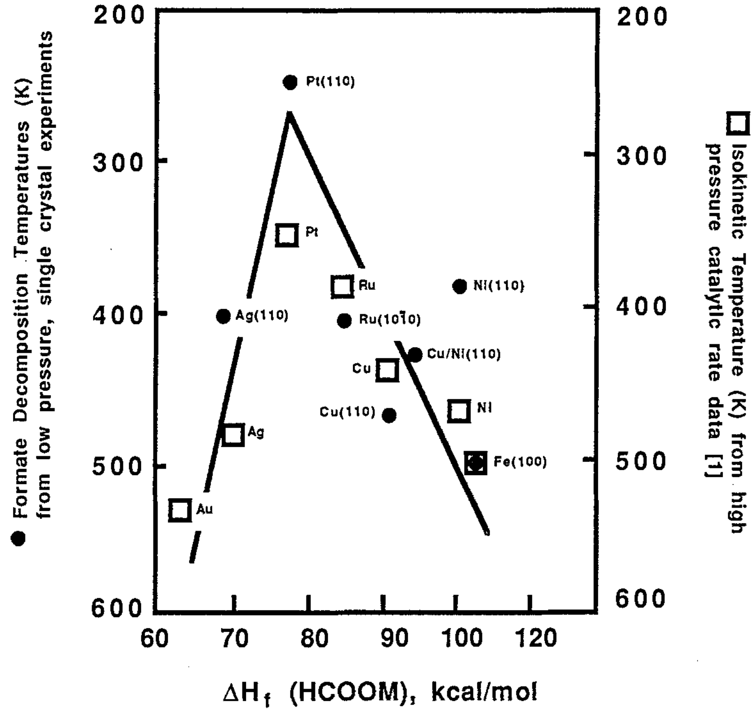

Fig. 1. Volcano plot for HCOO decomposition, redrawn from ref. [3].

namics of formation of metal-formate or metal-oxygen bonds on the IBs, because of the weakness of M–H bonds on the IB metals. Since formate decomposition on these metals occurs via cleavage of the C–H bond, a low affinity of the metal surface for hydrogen atoms would increase the thermodynamic and kinetic barriers to formate decomposition. Although this explanation is qualitatively correct, the "volcano" of formate stabilities is rather misleading. Fig. 2 illustrates a plot of formate decomposition temperatures from TPD experiments on single crystals [4–15] vs. the enthalpies of formation per mole of metal of the corresponding metal oxides (Tanaka-Tamaru plot). It is apparent that the IB metals do not represent the complementary leg of the "volcano" to the Group VIIIs; rather they give a parallel but separate family of points vs. the Group VIII metals. The two lines in fig. 2 for the peak temperatures (T_p) for formate decomposition are given by the equations

$$\text{(Group VIII)} \quad T_p(\text{K}) = 2.54\left[-\Delta H^0_{f\text{MO}}\ (\text{kcal/mol})\right] + 216 \tag{1}$$

$$\text{(Group IB)} \quad T_p = 2.63\left[-\Delta H^0_{f\text{MO}}\right] + 384. \tag{2}$$

If one makes the additional assumptions that the pre-exponential factor is 10^{13} s^{-1} and all data were obtained at a constant heating rate of 10 Ks^{-1}, the linear

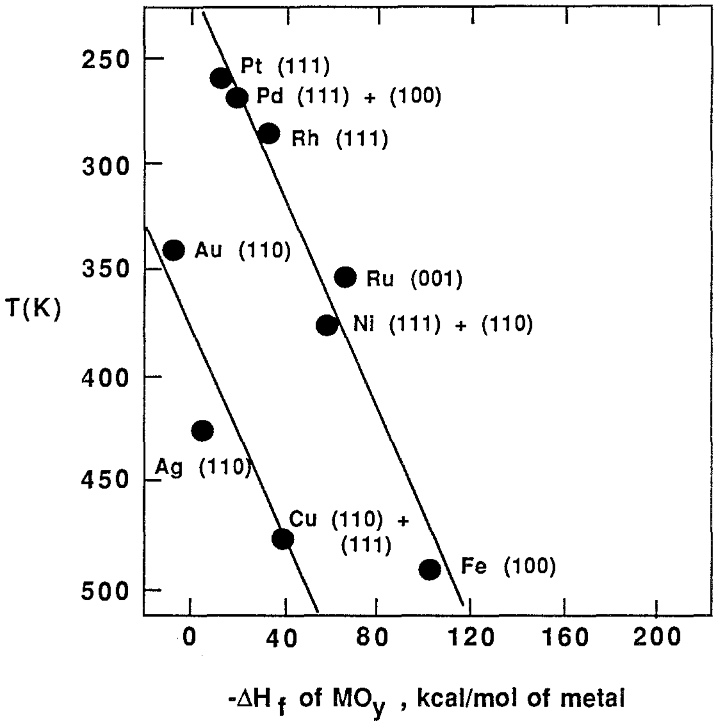

Fig. 2. Formate decomposition temperatures.

free energy relationships become

$$\text{(Group VIII)} \quad E_a\ (\text{kcal/mol}) = 0.157\left[-\Delta H^0_{f\text{MO}}\right] = 12.66 \tag{3}$$

$$\text{(Group IB)} \quad E_a = 0.162\left[-\Delta H^0_{f\text{MO}}\right] + 23.0. \tag{4}$$

The ca. 10 kcal/mol offset in E_0 reflects the lower affinities of the IB metals for hydrogen atoms and the correspondingly higher barrier for hydrogen transfer from the carboxyl carbon of the formate to the metal surface. The following conclusions may be drawn from the correlations illustrated in fig. 2.

1. The same linear free energy relationship cannot be applied to formate decomposition on the Group VIII and IB metals; in effect it is dangerous to generalize from the IBs to the VIIIs. This has clear implications for comparative activities, and as shown below, for reaction selectivities as well. It is unfortunate in that, as pointed out by Madix [16], many of the surface intermediates of interest can be synthesized most cleanly by proton transfer to preadsorbed oxygen atoms on the IB metals.

2. For the simple C–H cleavage involved in formate decomposition, a single linear free energy relationship can be applied to describe the kinetics of formate decomposition on all of the Group VIII metals. Data obtained on different

crystallographic planes of a given metal suggest that the influence of surface structure on formate stability is minimal. Moreover, it is likely that in the absence of significant steric effects, whatever crystallographic influences exist on formate stability will also be reflected in the atom binding energies which one might prefer to use over bulk oxide thermodynamics. Thus a single LFER would still be applicable for the Group VIII metals, with little variation for different surface structures. This is quite consistent with the traditional view of catalysis by metals, which considers the activation of O–H and C–H bonds characterizing the decomposition of formic acid to be facile, structure-insensitive reactions [17].

Strikingly similar conclusions may be drawn for the decomposition of the simplest alcohol, methanol, on surfaces of the Group VIII and IB metals. HREELS and isotopic labelling experiments have shown that methanol decomposition proceeds by initial cleavage of the O–H bond on these metals to form stable methoxy (CH_3O) intermediates. This reaction occurs readily between 100 and 200 K on the Group VIII metals. The IBs generally require the addition of oxygen atoms to the surface to facilitate methoxy formation by proton abstraction (although this can be avoided on Cu by the use of higher adsorption temperatures [18]). In any case, one can form isolable CH_3O species on all of these metals (albeit with somewhat greater difficulty than for formates) and can track their decomposition by HREELS, TPD, etc. Fig. 3 illustrates the "volcano" plot for CH_3O decomposition, using literature values [18–34] for CH_3O decom-

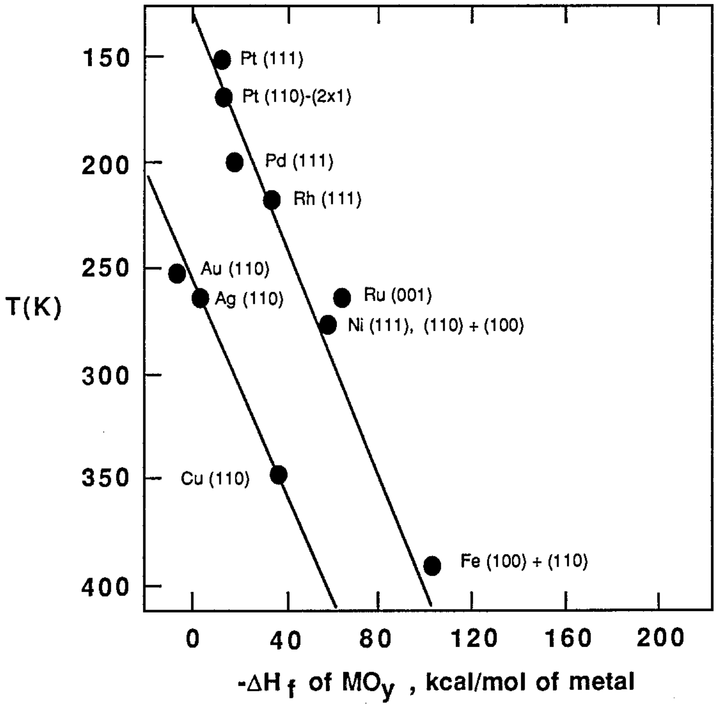

Fig. 3. Methoxide decomposition temperatures.

position temperatures. The similarity to the plot (fig. 2) for formate decomposition is remarkable. Once again we see essentially two linear correlations of decomposition temperature with enthalpy of formation of the metal oxide; one line for the Group VIII metals and one line for the IBs. Moreover the slopes of these lines are in excellent agreement with those of fig. 2 for formate decomposition; those for CH_3O decomposition are simply offset to lower temperature by ca. 80 K (on the Group VIII metals). The fits to the CH_3O data, corresponding to the analysis of formate decomposition above are

Group VIII:

$$T_p\ (K) = 2.54[-\Delta H^0_{fMO}\ (kcal/mol)] + 132 \qquad (5)$$

$$E_a\ (kcal/mol) = 0.157[-\Delta H^0_{fMO}] + 7.47 \qquad (6)$$

Group IB:

$$T_p = 2.24[-\Delta H^0_{fMO}] + 261 \qquad (7)$$

$$E_a = 0.138[-\Delta H^0_{fMO}] + 15.4. \qquad (8)$$

If one considers the displacement along the x-axis required to superimpose the CH_3O and HCOO decomposition temperatures for the Group VIII metals, one obtains an offset of 33 kcal/mol in the value of ΔH_{fMO} used as a correlating parameter. This represents essentially the difference in the enthalpy of formation of $HCOO\cdot$ vs. $CH_3O\cdot$, which can be determined from thermochemical data [35] to be 31.6 kcal/mol. Although this is an oversimplification since we have considered neither actual ΔH_f data for metal formates and methoxides, nor the product distribution from the decomposition of these species, this difference suggests that the difference in formate and methoxide stabilities results essentially from the shallower thermodynamic well characteristic of the methoxide. In effect the transition states for hydrogen abstraction from these two simple adsorbates are quite similar, and one could, in principle, construct a single linear free energy relationship which included both methoxides and formates, if data on the enthalpies of formation of each on different metals were available.

As noted above, decomposition of methoxides on the Group IB metals requires a different correlation than on the Group VIIIs. As with the formates, one sees a lower affinity for hydrogen atoms on the part of the IB metals, and a correspondingly greater thermal stability of the organic moieties from which they might be abstracted. There is also a significant difference in the *selectivity* of CH_3O decomposition between the Group VIII and IB metals, to understand which one must consider the details of the sequence of C–H cleavage reactions. On the IB metals, the principal product of CH_3O decomposition observed in TPD experiments is formaldehyde, an unsurprising result since these metals were the first catalysts for the selective oxidation of methanol to formaldehyde. In contrast, on the Group VIII metals, in the absence of surface modifiers such as sulfur or oxygen, formaldehyde is never observed in methanol TPD; dehydrogenation goes to completion and the sole products are CO plus H_2. The production of CO and H_2 suggests that methoxide decomposition proceeds via a sequence of dehydrogenation reactions, the first of which would produce formaldehyde on the surface. This has been confirmed both by experiments utilizing the kinetic isotope effect to demonstrate the rate determining cleavage of the methoxide C–H bond on Ni(111) [31], and by careful HREELS studies which have isolated adsorbed formaldehyde species in the course of methanol decomposition on Pd(111) [36]. However, in contrast to its behavior on the IB metals, this intermediate dehydrogenation product, formaldehyde, never leaves clean surfaces of the Group VIII metals intact. The reason is that formaldehyde (and carbonyl compounds in general) are bound differently on the two. On the IB metals, aldehydes and ketones bind weakly via donation of the lone pair electrons from the carbonyl oxygen to the metal surface in an η^1(O) configuration. On clean surfaces the Group VIII metals aldehydes and ketones are bound in an η^2(C, O) configuration, with the carbonyl axis nearly parallel to the surface and with the $C=O$ bond strongly rehybridized. (The red shift of 300–400 cm^{-1} for the ν(CO) mole of η^2 species relative to the free molecules is easily detected by HREELS [37]). These η^2-aldehydes are strongly bound to the surface and their further dehydrogenation is strongly favored over desorption; aldehydes are not observed as volatile products of alcohol dehydrogenation on the Group VIII metals. We have shown that on Pd(III) this strong rehybridization of the carbonyl group can be poisoned by the presence of electronegative surface modifiers such as oxygen [38,39]. In this case the bonding reverts to η^1(O), the activation energy for desorption is lowered by ca. 5 kcal/mol, aldehyde desorption can compete kinetically with decomposition, and aldehydes are observed as volatile products. With respect to aldehyde binding configuration and desorption, then, electronegative modifiers make the platinum group metals "look" more like their more noble neighbors.

The analysis above suggests that the decomposition of methanol via methoxide and formaldehyde intermediates on transition metal surfaces is straightforward. The sequence of dehydrogenations is the same in all of the examples cited; the stabilities of methoxides on different metals are predicted by a simple linear free energy relationship. Dehydrogenation is facile and structure-insensitive as expected. The selectivity of methanol decomposition can be understood by consideration of the nature of the interaction of the intermediate dehydrogenation product, formaldehyde, with different metal surfaces. However at this point it is worthwhile to consider the caution with which one should approach the above correlations, as well as the potential pitfalls they suggest in the interpretation of conventional "volcano" plots of catalytic rate data.

Several recent reports [23,40–42] have suggested that methanol or methoxide species on platinum and palladium surfaces can react via C–O scission to produce adsorbed methyl groups and/or methane, rather than dehydrogenation products. Although this reaction has proven difficult to verify on the Pd(111) surface [43,44] its occurrence on other surfaces cannot be ruled out. The data included in fig. 3 which form the basis for equations (5) and (6) do not include any examples of C–O scission. Therefore the above conclusions regarding methanol dehydrogenation may not apply to methanol deoxygenation. The latter reaction may not obey the same linear free energy relationship as the former; moreover, the C–O scission reaction may be structure sensitive, as suggested by Wang and Masel [23].

With that caveat, the LFERS depicted in figs. 2 and 3 have important consequences for the interpretation of the catalytic activities of different metals. It is clear that "volcano" plots for Group VIII metal-catalyzed reactions can be extended beyond these elements in a qualitative, but not quantitative fashion. Figs. 2 and 3 clearly show different correlations for dehydrogenation of surface intermediates on the Group VIII vs. the IB metals. Limited data available for formate and methoxide decomposition on Group VI metals [24,25,34] suggest that these would also fall outside the correlation for the Group VIIIs, although caution is required as the surfaces of early transition metals often contain adsorbed oxygen and carbon atoms from prior unselective decomposition of reactants such as formic acid or methanol. In any case, it is clear that conclusions regarding the facile or demanding nature [17] of metal-catalyzed reactions should be based upon activity variations within Group VIII, and not beyond.

The data above suggest that one must also be careful in the explanation of "volcano" behavior for catalytic reactions on different metals. The conventional interpretation of Balandin volcano plots suggests that there is a shift in the rate-determining step as one crosses the peak: the rate determining step on the "left" slope is the formation of the surface intermediate; on the "right" slope it is the decomposition of that intermediate. While this interpretation is likely to be correct *within* any family of metals which exhibit volcano behavior, it may not hold for jumps across columns of the Periodic Table. For example, from the data illustrated in figs. 1 and 2, it appears that there is a shift in the rate-determining step for formic acid decomposition on the IB metals. The isokinetic temperatures for formic acid decomposition on Cu and Ag are essentially equal to the respective peak temperatures for formate decomposition, suggesting that this is the rate determining step of the catalytic reaction on these two metals under the conditions measured. The isokinetic temperature for formic acid decomposition on Au is nearly 200 °C higher than the formate decomposition temperature, suggesting that formate formation is rate-determining on this metal. The "volcano" illustrated in fig. 1 for Group VIII + IB metals combined would lead one to the correct conclusion regarding the rate determining step on Au or Cu, but not Ag. Failure to recognize that the Group VIII and IB metals belong on different "volcanoes" would lead to exactly opposite strategies for catalyst promotion. Surface modifications (e.g., alloying) which would allow one to interpolate between the thermodynamic properties of adsorbates on silver and copper would be predicted to produce a catalyst more active than either of these according to the volcano depicted in fig. 1, but would actually produce a monotonic change in activity from copper to silver if the decomposition of a common surface intermediate were rate determining in all cases. Again one must be careful to establish whether a single linear free energy relationship can be applied to all of the catalysts of interest for a given reaction.

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