GENERAL DISCUSSION

Dr J. A. H. MacBride (University of Durham) (communicated): In addition to my comments on the paper by Bond et al., two further comments arise from the mechanisms presented by Dr Serwicka. First, when molecular orbitals have contributions from two or more inequivalent atoms which are potential sites for reaction, in which the MO is the 'frontier' orbital (e.g. the HOMO of a nucleophile), the atom with the highest coefficient in the ground-state is not necessarily the site of fastest reaction. This arises, of course, because the MOs may be so perturbed as reaction proceeds that the ground-state calculations do not predict the relative activation barriers correctly. Furthermore, this approach is inapplicable if equilibrium between the products (of some step) is attained, as might be the case for methylation on bridging or terminal oxygen atoms of the Keggin structure. The conclusion that the Keggin-oxygen is behaving as a nucleophile in the rate-determining step of oxidation also seems open to question.

The second point concerns the mechanism of oxidation of alkenes to maleic anhydride. It is not necessary to infer a furan derivative as intermediate since maleic acid forms its anhydride\(^2\) (in the absence of dehydration catalyst) at 200 °C (and its trans isomer at a somewhat higher temperature) so that cyclisation after oxidation is not improbable. Preference for C\(\text{\textgreek{x}}\)-terminally oxidised products (all leading to maleic anhydride) may be due to preferential (radical) oxidation of positions adjacent to an initial non-terminal double bond (allyl positions) and to preferential formation of a double bond (by oxidation-dehydration, or dehydrogenation) conjugated with an initial carbonyl function:

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{C}=\text{O} & \quad \text{C}=\text{O} \\
\text{X} & \quad \text{X}
\end{align*}
\]

\(\text{*radical stabilised positions}
\]

\(\text{X} = \text{alkyl, H, or OH}\)


Dr E. M. Serwicka replied: Any mechanism postulated should take into account the available experimental evidence. In the case of methanol interaction with the Keggin unit, adsorbed protonated methanol [II, fig. 9, p. 185] has been detected with PAS-FTIR\(^1\)
and $^{13}$C m.a.s. n.m.r.\textsuperscript{2} identified methylation of bridging oxygen sites (III, fig. 9). Additionally, e.s.r. i.r.\textsuperscript{3} and TPD\textsuperscript{4} data on methanol interaction with the Keggin unit indicate that major reaction steps have threshold temperatures. At $T < 453$ K methanol chemisorption with the electron transfer to the Keggin unit occurs to give an e.s.r. signal typical of a reduced but not oxygen-deficient Keggin anion, with the characteristic Keggin i.r. spectrum virtually unperturbed (V, fig. 9). There is no measurable formaldehyde evolution at this stage (TPD). At higher temperatures, desorption of formaldehyde (TPD) occurs which leaves behind the Keggin unit containing a bridging oxygen vacancy (i.r.) at which a trapped electron gives a characteristic e.s.r. signal\textsuperscript{3-5} (VI, fig. 9). Any mechanism alternative to that proposed by us would have to deal with these facts. The mechanism you suggest (see comments on the paper by Bond et al.) is basically similar to ours, except for the transfer of electrons rather than the transfer of protons in the initial step. Our intention was to emphasise that the Keggin unit has strong acidic properties and the proton affinity of methanol will be the driving force to form the adsorbed methyl oxonium moiety. Configuration IV is the only one in our scheme that lacks direct experimental support and as such remains speculative. However, transition III $\rightarrow$ V in fig. 9 requires a proton abstraction and a transfer of two electrons to the Keggin unit. This concerted operation may be presented as proceeding in two steps, the first being an attack of the Keggin bridging oxygen lone pair (HOMO) on the methoxy group LUMO localized predominantly on the CH$_3$. In view of the antibonding character of the latter this weakens the C—H bond and enables a facile proton transfer to give a virtual configuration, IV, which will rapidly reform, releasing excess electrons to the catalyst via the carbon—oxygen $\pi$-system, to end up as configuration V.

Concerning the applicability of a HOMO—LUMO approach we are aware of its limitations but in the present case the theoretically predictable reaction pathways agree well with those observed experimentally, indicating the usefulness of such considerations.

3 E. M. Serwicka, unpublished results.

**Dr J. C. Vedrine** (Institut de Recherches sur Catalyse, CNRS, Villeurbanne, France) said: You have made theoretical calculations of LUMO and HOMO orbitals of CH$_3$OH adsorbed on bridging oxygen atoms of your Keggin unit which helps you to propose a reaction mechanism for oxidation into HCHO. However you have to make the assumption that terminal $\equiv$Mo=O oxygens are inactive. I would have liked a theoretical approach without such an assumption. My question is therefore to know if you have made the calculation for CH$_3$OH adsorption on Mo=O oxygen. If so, are the molecular orbitals very different?

**Prof. R. A. van Santen** (University of Technology, Eindhoven, The Netherlands) commented: I would like to point out that the predicted reactivity of bridging O species agrees with the results of Pauling's valency rules. I would like, to ask whether it would not be better to study clusters containing Mo as well as V, since the acidic proton coordinated to the bridging oxygen is generated by vanadium. If one were to apply thermodynamic arguments, which of the oxygens (bridging or monocoordinated) would be most active?

**Prof. J. Haber** replied: From the solution $^{17}$O n.m.r. study\textsuperscript{1} it can be inferred that introduction of vanadium leads to an increased electron density on bridging oxygens as compared to the unsubstituted 12-molybdophosphate anion but of the two options it is the bridging oxygen of the Mo—O—Mo type rather than Mo—O—V type that
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carries higher charge. Therefore in our mechanistic scheme we include Mo centres only.
Nevertheless, calculation of the electronic structure of a V-substituted Keggin anion
would certainly improve the validity of discussed HOMO-LUMO interactions.

Prof. V. Ponec (Gorlaeus Laboratories, Leiden University, The Netherlands) suggested:
According to your mechanism all oxygen in formaldehyde molecules originates from
the oxide lattice and not from CH₃OH. Perhaps, the validity of this conclusion can be
checked by using CH₃¹⁸O. The exchange reaction of H₂¹⁸O with the oxide probably
spoils it, but the ¹⁸O/¹⁰O ratio in CH₃O could also be informative with such a complica-
tion, for example, if one of the extreme values (zero or ∞) were found.

Prof. Haber responded: In view of the heteropolyacid ability to exchange rapidly
bulk oxygen with water vapour¹ (at 523 K 80% of O atoms within 1 h), it would be
difficult to design a sensible experiment with labelled molecules. In our opinion, the
use of ¹⁸O-labelled catalyst, rather than CH₃¹⁸OH could provide the unequivocal answer.

Prof. J. B. Nagy (FUNDP, Namur, Belgium) asked: You have emphasized that the
methyl group should be attached on the bridged oxygen rather than on the terminal
oxygen in heteropolysalts. Is the difference in energy between these two forms high
enough? If not, at higher temperatures, a random distribution of the methyl groups
between the two types of oxygen could occur due to the mobility of the methyl groups.

Prof. Haber answered: On increasing temperature only bridging oxygens are extracted
from the Keggin anions (i.r., e.s.r.). This makes us believe that the mobility of methyl
groups, also at elevated temperatures, is limited to the network of the Keggin bridging
sites.

Dr G. J. Hutchings (University of Liverpool) said: In the proposed mechanistic scheme
for methanol conversion over heteropolyacid catalysts (your fig. 9) it is proposed that
the methanol interacts with the Keggin unit to produce a methyloxonium compound
(III). It is proposed that intermediate III is subsequently deprotonated by an adjacent
oxygen to form a methylene oxonium ylide type intermediate (IV). In our studies of
methanol conversion to hydrocarbons over the pentasil zeolite H-ZSM-5 we have
proposed similar intermediates in the formation of the initial carbon–carbon bond.¹²
By analogy with organometallic chemistry it would be considered that structures such
as intermediate IV would be very reactive to gas-phase oxygen. In this case it would
be gas-phase oxygen and not lattice oxygen that would be incorporated into the product
formaldehyde. It is possible to comment on this possibility?

Prof. Haber responded: Indeed, our mechanism is formally similar to that proposed
in your studies of the C–C bond formation on ZSM-5. However, a basic question may
be raised as to whether the species presented as IV in fig. 9, interacting with a transition-
metal oxide system can be considered as analogues of ylide structures appearing at the
surface of a zeolite catalyst. At variance with oxides of main group elements, empty
levels in the d-band are present in the transition-metal oxide catalyst. Therefore, any


excess negative charge on the carbon atom will be immediately transferred to the d-band making the transient ylide-like structure short-lived. The resulting methene group will be much less prone to the attack by molecular oxygen.

Prof. G. Centi (Department of Industrial Chemistry and Materials, Bologna, Italy) remarked: My question regards the role of V in the heteropolyacids, with specific reference to the selective transformation of alkanes. We are working on this problem, but our preliminary results indicate a more complex situation than that which you outlined. When all the vanadium is inside the Keggin structure in substitution of Mo the heteropolyacid is not very active in butane oxidation. The activation of butane requires the presence of some V sites in a cationic position, external to the Keggin unit. These results indicate a direct participation of V sites in the mechanism of activation of butane, and not only in the modification of electron density of bridging oxygen as you suggested. In our opinion the mechanism is not very different from what is observed for V-P oxides\(^1\) on which experiments with labelled molecules\(^2\) clearly indicate that the H atoms are abstracted from carbon atoms 2 and 3 and not 1 and 4. Have you other evidence regarding your hypothesis of the mechanism of alkane activation on V-heteropolyacids?


Prof. Haber replied: The suggested way of activation of alkanes over heteropolyacids is an attempt to employ reasoning along the line of possible HOMO–LUMO interactions. At present there is no experimental evidence that it is indeed the operating reaction pathway. Nevertheless, as you certainly remember, our common work on selective oxidation of pentane [ref. (8), p. 1871 has shown that there is a striking difference in the behaviour of a V-substituted heteropolyacid and a standard V–P–O catalyst. The former gives exclusively maleic anhydride, the latter a mixture of phthalic and maleic anhydrides. In view of this, one has to be very cautious in using a per analogiam argument in mechanistic considerations concerning both systems. Clearly, a detailed study, preferably with labelled molecules, is required to elucidate this problem.

Finally, Prof. J. B. Moffat (communicated): The equation provided by you

\[
\sigma_{\text{An}-G} > \sigma_{\text{V,0,2--G}} \cos \theta + \sigma_{\text{V,0,3--An}} \cos \theta
\]

appears to be a modified version of the Young–Dupré equation. However, it is questionable whether the assumptions implicit in the Young–Dupré equation, namely those which lead to the disappearance of the Gibbs surface chemical potentials, are valid in the system under study. Would you care to comment?

Prof. Haber, in response, said: From the thermodynamic point of view the situation at the solid/solid/gas line is fully analogous to that assumed for the solid/liquid/gas line and the same surface free-energy relationship as well as equilibrium condition operates in both cases. However, a rigorous derivation of the equivalent Young equation is not an easy exercise in the former case. As in the description of thin-oxide layers we are interested mainly in predicting the evolution of the system with time, it is more convenient to use the concepts of the work of cohesion and adhesion and describe spreading as proceeding when the energy of adhesion of the mobile phase to the immobile support is greater than its energy of cohesion.

Prof. W. Palczewska (Polish Academy of Sciences, Warsaw, Poland) asked the first question on Prof. B. Nagy’s paper: Could you specify the kind of reaction used and
Table 1. Size of the Ni$_2$B particles synthesized from CTAB–hexanol–water microemulsions

<table>
<thead>
<tr>
<th>[Ni(II)] x 10$^2$/mol kg$^{-1}$</th>
<th>$d^a$/Å</th>
<th>$\sigma^b$/Å</th>
<th>n$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB(12.0%)-hexanol (80.0%)-water (8.0%)</td>
<td>2.5</td>
<td>31</td>
<td>4</td>
</tr>
<tr>
<td>CTAB(18.0%)-hexanol (70.0%)-water (12.0%)</td>
<td>5.0</td>
<td>32</td>
<td>4</td>
</tr>
</tbody>
</table>

$^a$ Average diameter of the particles; $^b$ standard deviation; $^c$ number of measured particles.

the temperature range for the catalytic activity of the metal-boride particles? Did you examine the influence of boron on the catalytic activity?

Prof. J. B. Nagy replied: We essentially checked the hydrogenating activity of the boride particles in the liquid phase at room temperature. In order to increase the temperature, the particles should be deposited on a support to prevent coagulation. We are currently working on the problems using Pt and Pt–ReO$_2$ particles.

Two patents are also available in the literature using deposited colloidal monodisperse particles. In the first case, the deposition of the particles on a support follows their preparations in the microemulsion. In this case, however, a broad metallic size distribution is obtained, due to the agglomeration during impregnation or transfer onto the surface of the support and a requisite thermal stability cannot be achieved. The second method consists of reducing the metal ions directly on the surface of the support after impregnation of the microemulsion. In the latter case, the microemulsion components are eliminated by evaporation and helium purge.

The influence of boron on BO$_2^-$ on the surface of the metal-boride particles was not examined systematically with respect to the catalytic activity of the boride particles and, unfortunately, I cannot comment further on this topic.

Prof. J. M. Thomas (The Royal Institution, London) then said: The dispersity of the particles shown on your transparency is 5–10 Å. Are they really monodisperse?

Prof. J. B. Nagy answered: Indeed, the dispersion of the particles shown by the transparency is within 5–10 Å. The smallest distribution obtained is 4 Å as shown by table 1 [ref. (16) of our paper]. It has to be noticed that the size-distribution is comparable to previously reported values [ref. (11) of our paper].

Dr P. A. Sermon (Brunel University, Uxbridge) (communicated): Your colloidal routes to metal borides in microemulsions use excess NaBH$_4$. Were you able to: (i) vary the Me/B ratio, (ii) remove CTAB and NaBH$_4$ contaminants, and were the surfaces so produced homogeneous?

Prof. B. Nagy responded: (i) The excess NaBH$_4$ used over MCl$_2$ (M = Ni and/or Co) is ca. three-fold. When a higher excess was used, it did not influence the particle size, whereas a lower excess led to imperfect reduction of the metal ions. The excess is necessary, because part of the NaBH$_4$ reagent is hydrolysed even at a temperature close to 0°C.
(ii) The strongly adsorbed contaminants are CTA\(^+\), Br\(^-\), Cl\(^-\) and B(OH\(_2\))\(^-\) ions. The washing procedure to eliminate most of these ions is described in the text. Nevertheless, BO\(_2\)\(^-\) contaminant still remains on the surface, together with the NiO and CoO oxides, stemming from the easy oxidations of the highly reactive boride particles.

The Ni\(_2\)B, Co\(_2\)B and Ni—Co—B particles thus prepared are amorphous, the mixed particles do contain both Ni and Co atoms, and they do not correspond to a mechanical mixture of separate Ni\(_2\)B and Co\(_2\)B particles. Two pieces of evidence strongly support this hypothesis. (a) The nucleus of the particle is essentially made of Co\(_2\)B, hence the outer rim does contain more Ni\(_2\)B entities (see text); (b) the catalytic hydrogenation of crotonaldehyde as a function of bulk Ni content does not follow the strict proportionality curve, but it shows a slightly higher activity, especially for low Ni content, which is attributed to the surface enrichment in Ni\(_2\)B [ref (15) of our paper].

These results also show clearly, that the particles are not homogeneous.

Prof. M. W. Roberts (University of Wales College of Cardiff) asked: Do you have any information regarding the oxidation state of ‘nickel’ in the nickel borides from the Ni(2p) spectra? This together with the valence-band density of states might throw some light on the high catalytic activity of NiB.

Prof. B. Nagy replied: The X.p.s. spectra of Ni in Ni\(_2\)B show a certain degree of charge transfer from boron to nickel\(^{1,2}\). Indeed, the binding energy of boron in Ni\(_2\)B is increased \((E = 187.7 \text{ eV})\) with respect to the element B \((E_b = 186.2 \text{ eV}^3, \text{ and } E_b = 187.3 \text{ eV}^4)\). In contrast, the binding energy of Ni is decreased: \(E_b = 851.7 \text{ eV with respect to Ni metal (} E_b = 852.1 \text{ eV}^3 \text{ and } E_b = 852.7 \text{ eV}^5\) (fig. 1). The higher electron density on Ni in Ni\(_2\)B could also explain the higher activity of Ni\(_2\)B with respect to Ni metal.


Prof. P. B. Wells (Hull University) commented: The presence of Cl\(^-\), Br\(^-\), BO\(_2\)\(^-\) ions adsorbed on the metal particles can be distinguished by using the hydrogenation reaction
of either buta-1,3-diene or isoprene. In the presence of Cl$^-$, Br$^-$ ions 1,4-addition is favoured, while 1,2-addition predominates without these ions.

Prof. B. Nagy responded: Thank you for your comment concerning the detection of Cl$^-$ and Br$^-$ ions adsorbed on the metal-boride particles. The hydrogenation of buta-1,4-diene (or of isoprene) could be used and the products would be but-2-ene, in the presence of Cl$^-$ and Br$^-$ ions (1,4 additions), and but-1-ene in the absence of these ions (1,2-addition). It certainly would be very interesting to check.