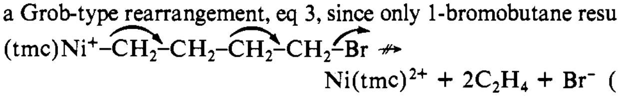
Table I. Reactions[a] of $(tmc)Ni(CH_2)_4Y^+$ Ions with $Ni(tmc)^+$ and with H_2O

$R{-}Ni(tmc)^+$, R =	with $Ni(tmc)^+$ product	with $Ni(tmc)^+$ $k/M^{-1}\,s^{-1}$ [b]	hydrolysis product	hydrolysis k_{hyd}/s^{-1} [c]
$-(CH_2)_4I$	C_2H_4		$I(CH_2)_3CH_3$	2.7×10^{-2}
$-(CH_2)_4Br$	C_2H_4	1.6×10^3	$Br(CH_2)_3CH_3$	1.3×10^{-2}
$-(CH_2)_4Cl$		$(\leqslant 10^1)$	$Cl(CH_2)_3CH_3$	0.8×10^{-2}
$-(CH_2)_4OH$	nr	$<10^{-2}$	$HO(CH_2)_3CH_3$	0.8×10^{-2}
$-(CH_2)_4OTs$	nr	$<10^{-2}$	$TsO(CH_2)_3CH_3$	0.8×10^{-2}
$-CH(CH_3)-(CH_2)_3Br$[e]	*d*		$[Br(CH_2)_4CH_3]$[e]	

[a] At 25.0 °C and 0.010 M NaOH. [b] Compare with $k = 1.5 \times 10^3$ $M^{-1}\,s^{-1}$ for 1-bromobutane and $k = 2.2$ $M^{-1}\,s^{-1}$ for 1-chloropropane. [c] Cf. k_{hyd} for $RNi(tmc)^+$ complexes (R = alkyl); the rate constants[6] lie in the range $(0.8–2.7) \times 10^{-2}$ s^{-1}. [d] Equal quantities of ethylene and propene, along with some *n*-pentane and 1-pentene from disproportionation of the 1-pentyl radical that results from reaction of the hydrolysis product (1-bromopentane) with $Ni(tmc)^+$ (see Scheme I). [e] Assumed from relative rates of 2° and 1° RBr's; smaller amounts of $(tmc)NiCH_2(CH_2)_2CH(Br)CH_3$ may be formed, hydrolyzing to 2-bromopentane.

complexes ($LM{-}(CH_2)_4{-}ML$; M = Co,[9-11] Rh;[12] L = N_4 macrocycle) are also observed, especially in reactions that proceed by nucleophilic (i.e., two-electron) pathways, and cyclobutane is formed in the reactions with *tert*-butyllithium.[13,14] Ethylene does result from reduction of 1,4-dibromobutane with lithium. A Grob-type rearrangement of $Br{-}(CH_2)_4{-}Li$ has been suggested.[15] In the case of $(tmc)Ni(CH_2)_3CH_2Br^+$, however, one can discount a Grob-type rearrangement, eq 3, since only 1-bromobutane results



$$(tmc)Ni^+{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}Br \not\rightarrow Ni(tmc)^{2+} + 2C_2H_4 + Br^- \quad (3)$$

from nickel–carbon bond hydrolysis, whereas ethylene requires the addition of $Ni(tmc)^+$ in at least trace quantities. A tetramethylene diradical, known[16] to undergo competitive cyclization and fragmentation, is also ruled out since no cyclobutane was observed here.

We suggest instead that ethylene formation is initiated by a second electron-transfer step, namely, the reaction between $Ni(tmc)^+$ and $(tmc)Ni(CH_2)_3CH_2Br^+$, eq 4.[17] This is supported

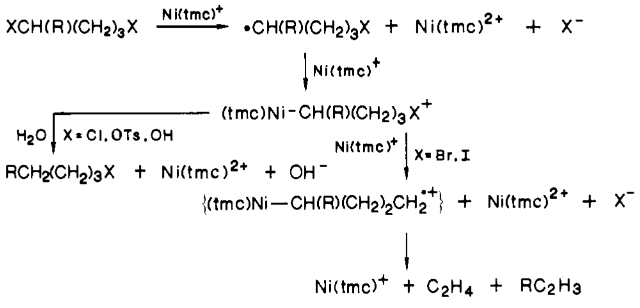
$$Ni(tmc)^+ + (tmc)Ni(CH_2)_3CH_2Br^+ \rightarrow BrNi(tmc)^+ + (tmc)Ni(CH_2)_3CH_2^{\bullet +} \quad (4)$$

by the similarity of the directly measured k_4 with rate constants for analogous bromine atom abstraction reactions[4] between $Ni(tmc)^+$ and bromoalkanes (Table II). It may be that a metallacyclopentane intermediate then intervenes and that ethylene is formed from it.

$$(tmc)Ni(CH_2)_3CH_2^{\bullet +} \rightarrow c\text{-}\{(tmc)Ni(CH_2)_4^{\ +}\} \rightarrow Ni(tmc)^+ + 2C_2H_4 \quad (5)$$

There is considerable precedent for metallacycle formation,[15,18,19] although this macrocyclic system is sufficiently sterically crowded about nickel that we must also consider an internal electron-transfer reaction with concerted C=C bond formation and Ni–C bond breaking, that avoids a cyclic intermediate. The subtle distinction requires the use of structurally rigid dihalides that will not permit metallacycle formation, as being planned at this time.

Scheme I[a]



[a] R = H, CH_3.

Table II. Rate Constants[a,b] for Halogen–Atom Abstraction Reactions between $Ni(tmc)^+$ and Substituted Halobutanes

halobutane	$10^{-3}k/$ $M^{-1}\,s^{-1}$	proposed $RNi(tmc)^+$ int., R =
$Br(CH_2)_4Br$	4.5[b,c]	$Br(CH_2)_4^-$
$CH_3CH(Br)(CH_2)_3Br$	4.3[d]	none
$Br(CH_2)_4Cl$	3.6[c]	$Cl(CH_2)_4^-$
$Br(CH_2)_4OTs$	*e*	$TsO(CH_2)_4^-$
$Br(CH_2)_4OH$	*e*	$HO(CH_2)_4^-$
$[M(CH_2)_4Br]^+$	1.6[c,f]	

[a] At 25.0 °C and 0.010 M NaOH. [b] Value is $k/2$, corrected statistically for comparison purposes. [c] Compare $k = 1.5 \times 10^3$ $M^{-1}\,s^{-1}$ for 1-bromobutane. [d] Compare $k = 2.8 \times 10^3$ $M^{-1}\,s^{-1}$ for 2-bromopropane. [e] Not determined. [f] M = $Ni(tmc)^+$.

Acknowledgment. This work was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under contract W-7405-Eng-82. Helpful discussions with Professors P. M. Warner, R. G. Bergman, C. E. Casey, and W. S. Trahanovsky are gratefully acknowledged.

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Holes in the Oxygen (2p) Valence Bands and the Concomitant Formation of Peroxide-like Species in Metal Oxides: Their Role in Metallicity and Superconductivity[†]

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Received June 15, 1987

Presence of electron holes in the valence bands of binary as well as complex copper chalcogenides has been recognized for sometime.[1-3] Holes in the valence bands of these compounds are induced by the presence of $Cu^{1+}(3d^{10})$ ions, giving rise to interesting structural distortions and electronic properties. Presence of such holes also explains[4] the instability of Fe_2S_3 with respect to FeS and FeS_2; here, electrons of S^{2-} origin create holes in the

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[†] Contribution no. 459 from the Solid State and Structural Chemistry Unit.
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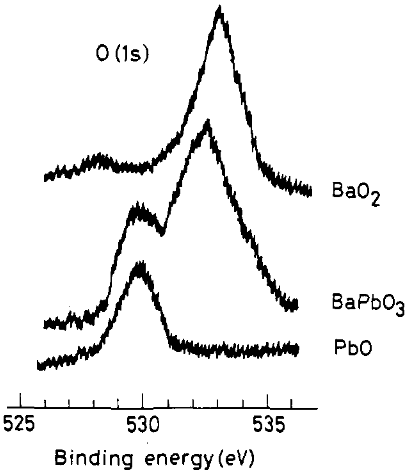

Figure 1. O(1s) spectra of PbO, BaO_2, and $BaPbO_3$.

valence band forming S_2^{2-} ions, by the transfer of electrons to the Fe^{3+} ions which then transform to Fe^{2+}. Although holes in the valence bands (VB) of sulfides and other chalcogenides forming S–S and other dimer bonds are commonly accepted, holes in the O(2p) VB of oxides leading to the formation of O–O bonds have not been invoked or their presence clearly established experimentally. We would expect the stability of the chalcogen VB holes to decrease in the order Te, Se, S, and O, since the holes occupy the antibonding states with respect to the dimer bond, in the top of the VB. We have investigated several oxide systems in an effort to explore for the presence of O(2p) VB holes forming peroxide-type units, the study being specially relevant to the mechanism of metallicity as well as high-temperature superconductivity in oxides such as $YBa_2Cu_3O_{7-\delta}$. The study has indeed yielded most interesting, though unexpected, results which are of considerable significance to the structure and properties of metal oxides.

In order to delineate O^{2-} and O_2^{2-} species in metal oxides, many of which are black specially when they are metallic, we have employed photoelectron spectroscopy.[5,6] The O(1s) binding energy of peroxide-like species (532–533 eV) has been established to be considerably higher than that of the oxide species (~530 eV);[5,6] HeII spectra show characteristic three-peak spectra (around 7, 10, and 13 eV) due to the σ_g, π_u, and $\pi_g{}^*$ molecular states of O_2^{2-} compared to a single peak around 5 eV in the case of O^{2-}.

In Figure 1, we show the O(1s) spectra of PbO and BaO_2 showing characteristic features of O^{2-} and O_2^{2-}, respectively. The O(1s) spectrum of metallic $BaPbO_3$ (recorded after unequivocally establishing its composition by means of the intensities of the metal core level peaks) shows peaks due to both O^{2-} and O_2^{2-}; HeII spectra also show the expected features. We have found a similar two-peak O(1s) spectrum in the case of $SrPbO_3$ which is a fairly good conductor, whereas insulating Sr_2PbO_4 shows only a single peak due to O^{2-}. The presence of O_2^{2-} in $Ba(Sr)PbO_3$ can only arise from the O(2p) VB holes. It is possible that valence fluctuation[7] of the type described by the following reaction occurs in oxides where the oxidation numbers of the metal ion (Pb in the present case) differ by two. We believe that such mixed

$$M^{n+} + 2O^{2-} \rightarrow M^{(n-2)+} + O_2^{2-}$$

valence is responsible for the metallic nature of $BaPbO_3$. We have obtained preliminary evidence for the presence of both O^{2-} and O_2^{2-} in the O(1s) spectra of $BaBiO_3$ and $BaBiPbO_3$ as well.

Oxygen excess $La_2NiO_{4+\delta}$ is a reasonably good conductor at room temperature and becomes metallic[8] above 500 K. We find the presence of peroxide species in this oxide which has generally been considered[8,9] to contain Ni^{3+}. X-ray absorption and X-ray photoelectron spectroscopy show no evidence for Ni^{3+}; on the other hand, presence of O_2^{2-} is clearly demonstrated by the characteristic O(1s) XPS peak. The composition $La_2NiO_{4.125}$ which is commonly found seems to be best represented by $La_2Ni^{2+}O_{3.875}{}^{2-}(O_2{}^{2-})_{0.125}$. The formation of the O(2p) VB holes in $La_2NiO_{4+\delta}$ is described by the reaction, $2Ni^{3+} + 2O^{2-} \rightarrow 2Ni^{2+} + O_2^{2-}$.

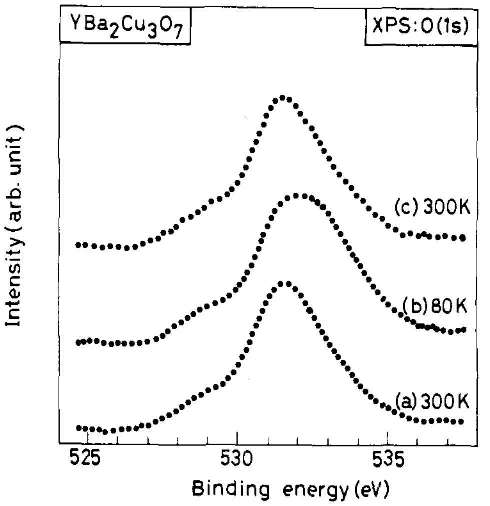

Figure 2. O(1s) spectrum of $YBa_2Cu_3O_7$ at (a) 300 K (b) 80 K and (c) on rewarming (b) to 300 K.

We have examined the chemistry of the high-temperature superconductor[10,11] $YBa_2Cu_3O_{7-\delta}$ showing zero-resistance in the 90–95 K range in some detail. Although stoichiometric samples of this oxide with $\delta \approx 0$ can be prepared, samples ordinarily prepared have δ in the range 0.15–0.65 giving an average oxidation state of copper between 1.9 and 2.2. X-ray absorption spectroscopy also confirms a similar range of oxidation states. A study of the thermogravimetric data in the light of the recent crystal structure[12,13] of $YBa_2Cu_3O_{7-\delta}$ has shown that the oxygens in the middle CuO layer consisting of strings of corner-shared CuO_4 polyhedra are crucial for the superconductivity. If one quarter of the oxygens from this middle CuO layer is removed, superconductivity is destroyed. Formation of O(2p) VB holes in the oxide would be associated with the formation of Cu^{1+} ions, and we have obtained clear evidence for such a phenomenon by means of electron spectroscopy.

In Figure 2 we show the O(1s) spectrum of $YBa_2Cu_3O_{7-\delta}$ recorded at 300 and 80 K; this figure also shows the O(1s) spectrum of the sample measured at 80 K after having been warmed to 300 K. While the spectra in parts a and c of Figure 2 are identical, the spectrum at 80 K in Figure 2b clearly shows a broadening on the higher binding energy side of the intense peak, indicating the growth of a new species at low temperatures. To understand the variation in the spectral shape quantitatively, we have analyzed the O(1s) spectra in terms of a combination of three Gaussians by a least-squared-error method. This analysis shows that at all temperatures there are three species of oxygen present with binding energies around 529.0, 531.5, and 533 eV. While the peak at 529 eV is due to the normal oxidic (O^{2-}) species, the peak at 531.5 eV can arise from the O^{1-} species and possible impurities such as OH^- and CO_3^{2-}. The most important observation is the existence of the peak around 533 eV which matches well with the binding energy of peroxide-like species. There is about 20% of the 533-eV species at 300 K, and its concentration

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increases to 40% at 80 K; the change is reversible. The intensity of this O(1s) feature due to the peroxide species increases progressively with decreasing temperature. This analysis shows that the O^{2-} and O^{1-} species are progressively converted into O_2^{2-} species as the temperature is lowered. We have also observed a progressive increase in the Cu^{1+} content with decrease in temperature as measured by the Cu(LVV) Auger line intensity. We believe that the formation of "resonating" O–O bonds due to hole–hole coupling may play a crucial role in the mechanism of superconductivity of this oxide.

Preliminary XPS measurements on the superconductor $La_{1.8}Sr_{0.2}CuO_4$ have shown that this oxide also exhibits the feature due to O_2^{2-} in the O(1s) region at 300 K which intensifies on cooling. This commonality between $YBa_2Cu_3O_7$ and $La_{1.8}Sr_{0.2}CuO_4$ is noteworthy.

Acknowledgment. We thank the Department of Science and Technology and the University Grants Commission for support of this research.

Chain-Carbonyl Transposition, an Alternative Strategy for the Synthesis of the 6,8-Dioxabicyclo[3.2.1]octanes: A Synthesis of the (±)-Brevicomins and Their Oxidative Cleavage to Tetrahydrofurans

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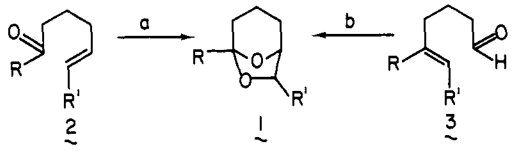
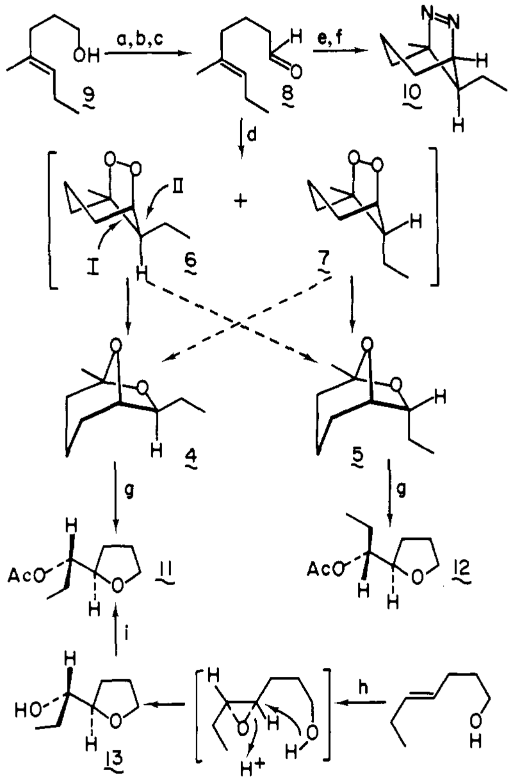
The 6,8-dioxabicyclo[3.2.1]octane system (**1** in Scheme I) has been perhaps the most widely synthesized unit in organic chemistry due to its widespread occurrence in nature[1] and the relative simplicity of many of the natural products that contain this unit. All of these syntheses have been based in actual fact or at least formally upon the corresponding acyclic olefinic unit **2** as outlined in strategy a of Scheme I.[2] In this work, we have developed an alternative strategy (b in Scheme I) which starts from a complementary acyclic olefinic carbonyl compound **3** and in which the carbonyl group and the olefinic terminal chain fragment become transposed during the course of the transformation.

This approach has been applied to the synthesis of *exo*- and *endo*-brevicomin, **4** and **5**, respectively, via the pivotal unsymmetrical endoperoxides **6** and **7** (Scheme II). The starting enal **8** is readily prepared from the alcohol **9**.[3] When enal **8** was subjected to conditions which previously had been used to produce the stable, symmetrical endoperoxide, 1,5-dimethyl-6,7-dioxabicyclo[3.2.1]octane,[4] the expected endoperoxides **6** and **7** could not be detected even when the reaction was conducted at −78 °C. Instead, **4** and **5** were formed directly in a ratio of 85:15.[5]

Scheme I



Scheme II[a]



[a] (a) Br_2, Ph_3P, Et_2O, 92%; (b) NaCN, DMSO, 88%; (c) DIBAL-H, Et_2O, 68%; (d) 70% H_2O_2, $BF_3{\cdot}Et_2O$, CH_2Cl_2, −78 to 0 °C, 14 h, 53%; (e) $TsNHNH_2$, Et_2O, 6 h; (f) $BF_3{\cdot}Et_2O$, room temperature, 2 h, 53% from **8**; (g) 70% H_2O_2, $BF_3{\cdot}Et_2O$, CH_2Cl_2, room temperature, 24 h, 83% for the formation of **11**; (h) *m*-CPBA, CH_2Cl_2, 70%; (i) Ac_2O, DMAP, Et_3N, CH_2Cl_2, 81%.

In an effort to prepare **6** and **7** by an independent route, the azoalkane **10** was prepared from enal **8** (Scheme II), and its sensitized photodecomposition studied in an effort to generate and trap the triplet 1,3-biradical with molecular oxygen.[4,6] While this approach did not lead to isolable quantities of peroxides,[7] the bicyclization of **8** to **10** proved most interesting in that only a single azoalkane isomer was formed. The absence of coupling[8] between the bridgehead proton and a syn proton on the one-carbon bridge in the ^1H NMR spectrum of **10** indicates that the ethyl substituent occupies this syn position. If the bicyclization of **8** with hydrogen peroxide displays a similar stereoselectivity,[9] then one might expect

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