

and bimetallic reduction processes play roles, the former prevailing at higher pressures.²³ When treated with ~ 2 equiv of C_2H_4 in a sealed NMR tube, **5** is quantitatively converted to the ethyl hydride, (silox)₃Ta(Et)H (**7**),²⁴ presumably the steric properties of **7** preclude further ethylene insertion.

Species **2a**, **2b**, **3**, **5**, and **7** represent a class of unusual metal hydrides that possess "hard" ancillary ligands.¹² The absence of bridging ligands in the postulated **2a**, **2b** structure is surprising in view of the propensity of hydride and alkoxide ligands to span two early metal centers.^{8,9,25} Perhaps the structure reflects the dominance of silox steric influences; alternatively, plausible μ -H units may ineffectively compete for orbitals utilized in strong silox $p\pi > d\pi$ donation. Clarification of such explanations must await an ongoing X-ray structure determination. Studies pertaining to the CO reduction products of **2a** and **3** and the reductive elimination pathways available to the hydride and alkyl hydride derivatives are future endeavors.

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(24) (silox)₃Ta(CH₂CH₃)H (**7**): ¹H NMR (C₆D₆) δ 1.29 (s, silox, 81 H), 1.82 (dq, CH₂, 2 H, $J = 3.2, 7.8$ Hz), 2.18 (t, CH₃, 3 H, $J = 7.8$ Hz), 22.30 (t, TaH, 1 H, $J = 3.2$ Hz).

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Can Nucleophiles Attack Radical Cations Directly? "Allowed" and "Forbidden" Polar Reactions¹

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As a result of Woodward and Hoffmann's pioneering work on pericyclic reactions,² the concept of "allowed" and "forbidden" reactions has become part of the language of organic chemistry. Till now, however, the terms have been restricted to just this class of reactions. Polar reactions, which constitute a large majority of organic reaction types, have never been classified in this way. In this paper we wish to demonstrate that the terms allowed and forbidden may be usefully applied to polar reactions as well. Within a family of polar reactions, e.g., nucleophilic addition, certain cases may be demonstrated to be intrinsically high-energy ones, i.e., forbidden, while in contrast others are low-energy reactions, i.e., allowed. The concept is illustrated by considering the reaction of radical cations and regular cations with nucleophiles, and a general rule enabling classification of polar reactions as either allowed or forbidden is provided.³

The reaction of nucleophiles with radical cations has been extensively studied over recent years^{4,5} and their low reactivity

(1) Presented in part at the ACS Symposium on "Nucleophilicity", Chicago, Sept, 1985.

(2) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim/Bergstr., W. Germany, 1971.

(3) The terms "allowed" and "forbidden", as employed in this paper, have the same practical consequences as in Woodward and Hoffmann's original treatment.² However, the theoretical roots are different. For pericyclic reactions the allowedness is based on symmetry considerations, while for polar reactions the selection is governed by just energetic considerations.

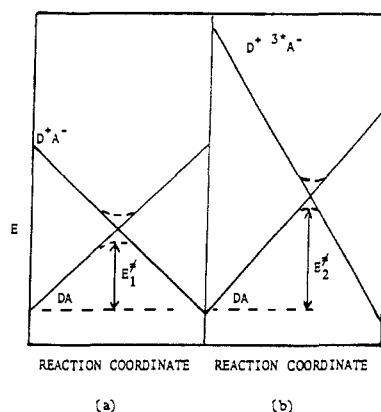
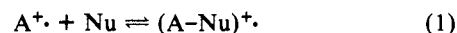


Figure 1. (a) Schematic energy diagram illustrating the way in which the reaction profile for nucleophilic attack on a normal cation may be built up from the avoided crossing of DA and D^+A^- configurations. (b) Corresponding diagram for nucleophilic attack on a radical cation, in which the product configuration is now $D^{+3}A^-$. Since $D^{+3}A^-$ is doubly excited with respect to DA, while D^+A^- is just singly excited, $E_2^* > E_1^*$.

noted by Ebersson.^{5a} One of the key mechanisms that has been proposed for these reactions, termed the half-regeneration mechanism,⁴ involves as a first step, direct attack of the nucleophile on the radical cation (eq 1). Such a process is consistent with



conventional organic chemical thinking and is readily represented by curly arrows. However, Parker^{4a,b} has recently reassessed existing data and concluded that in certain cases the half-regeneration pathway is not operative, as was initially thought. Alternative routes appear to be followed. It appears that disproportionation of the radical cation to the dication and the neutral precedes nucleophilic attack.^{4a,b,6} This is quite unexpected since the equilibrium constant for disproportionation is ca. 10^{-9} . The questions arise: *What inhibits direct nucleophilic attack on the radical cation? Why is it the dication and not the radical cation that reacts with the nucleophile?* We now demonstrate, using elements of the configuration mixing (CM) model,^{7,8} that direct nucleophilic attack on a regular carbocation is an allowed polar process while the corresponding attack on a radical cation is a high-energy pathway and hence a forbidden process.

All nucleophilic addition reactions may be thought of in terms of a $DA-D^+A^-$ avoided crossing. This is consistent with our recent discussion suggesting that much of organic reactivity may be

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(5) For a selection of papers on the reaction of radical cations with nucleophiles, see: (a) Ebersson, L.; Blum, Z.; Helgée, B.; Nyberg, K. *Tetrahedron* **1978**, *34*, 731. (b) Manning, G.; Parker, V. D.; Adams, R. N. *J. Am. Chem. Soc.* **1969**, *91*, 4584. (c) Shine, H. J.; Murata, Y. *Ibid.* **1969**, *91*, 1872. (d) Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368. (e) Parker, V. D.; Ebersson, L. *J. Am. Chem. Soc.* **1970**, *92*, 7488. (f) Marcoux, L. *Ibid.* **1971**, *93*, 537. (g) Svanholm, U.; Hammerich, O.; Parker, V. D. *Ibid.* **1975**, *97*, 101. (h) Svanholm, U.; Parker, V. D. *Ibid.* **1976**, *98*, 997, 2942. (i) Kim, K.; Hull, V. J.; Shine, H. J. *J. Org. Chem.* **1974**, *39*, 2534. (j) Evans, J. F.; Blount, H. N. *Ibid.* **1977**, *42*, 976. (k) Evans, J. F.; Blount, H. N. *J. Am. Chem. Soc.* **1978**, *100*, 4191. (l) Evans, J. F.; Blount, H. N. *J. Phys. Chem.* **1979**, *83*, 1970. (m) Hammerich, O.; Parker, V. D. *Acta Chem. Scand., Ser. B* **1981**, *35*, 341. (n) Cheng, H. Y.; Sackett, P. H.; McCreery, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 962. For a more extensive list of references, see ref 4.

(6) If the free radical cation undergoes disproportionation the mechanism is termed the disproportionation mechanism, while if the radical cation is first complexed to the nucleophile then the pathway is termed the complexation mechanism.⁴

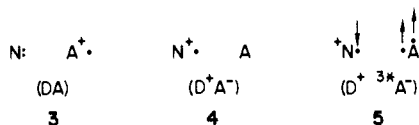
(7) For recent reviews of the CM model, see: (a) Pross, A.; Shaik, S. S. *Acc. Chem. Res.* **1983**, *16*, 363. (b) Pross, A. *Adv. Phys. Org. Chem.* **1985**, *21*, 99. (c) Shaik, S. S. *Prog. Phys. Org. Chem.* **1985**, *15*, 197.

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described in terms of a single electron shift.^{9,10} For a regular cation an electron shift from N: to R⁺ converts the electronic configuration describing reactants, the DA configuration, **1**, to



that describing the N-R combination product, D⁺A⁻, **2**. The case of a radical cation is, however, quite different. A single electron shift from the nucleophile to the radical cation A⁺ cannot lead to nucleophilic addition. Conversion of **3** to **4** by a single electron



shift (DA → D⁺A⁻) merely generates the parent hydrocarbon, A, together with N⁺. The absence of an odd electron on A after the electron shift precludes N⁺-A coupling, so that the net result of an electron shift, if it were to occur, would lead to just electron transfer.

Is direct nucleophilic attack on a radical cation then at all possible? The answer is yes, but the pathway is predicted to be a high-energy one and hence the term forbidden. The electronic configuration that describes the product of nucleophilic addition to a radical cation is shown in **5** and may be designated as D⁺³A⁻. The addition product, N⁺-A, is described by **5** since the odd electron on N may couple up with one of the uncoupled electrons on A to generate a covalent bond. Direct nucleophilic attack on a radical cation is therefore a high-energy process since **5** is doubly excited with respect to **3**. In order to transform **3** to **5**, an electron must be transferred from the nucleophile to the radical cation and then the latter excited to the triplet state. An energy diagram, Figure 1, schematically illustrates how a doubly excited product configuration, D⁺³A⁻, is expected to lead to a higher barrier¹¹ than a singly excited product configuration, D⁺A⁻. The idea that the energy of the excited state in part governs the barrier height for ground-state reactions is a central element of Marcus theory¹² and has been frequently applied in the quantitative application of the CM model.^{7c,8b,e} However, in these prior applications, it is a variation in the energy of a given excited state (D⁺A⁻) that was considered to affect the barrier height rather than an actual change in the identity of the excited state, as suggested here.

Of course, nucleophilic attack on the dication is predicted to take place readily. Formation of the radical cation species as a consequence of an electron shift from N: to A²⁺ leads to a N⁺·A⁺ radical pair which can collapse to give N⁺-A⁺. Similarly, reaction of a radical cation with a radical is also predicted to be a facile process. Here the electronic configuration of the reactants, A⁺·R, is identical with that of product so that in electronic terms the reaction is predicted to be barrier free.

In summary, viewing polar processes in terms of a single electron shift has far-reaching consequences. Our analysis suggests that polar processes, described by just a single electron shift (a DA-D⁺A⁻ crossing), may be classified as allowed, while those whose

products need to be described by a doubly excited configuration (e.g., D⁺³A⁻) may be classified as forbidden.³ Other reactivity problems also appear amenable to this simple theoretical treatment and will be discussed in a full paper.

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Synthesis and Characterization of a Confacial Bioctahedral Tantalum(II) Dimer with a Formal Triple Metal-Metal Bond

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Since the discovery of quadruple bonds between metal atoms an extensive chemistry involving dinuclear complexes with multiple metal-metal bonds has been developed for a number of transition elements.^{1,2} For the heavier group 5 metals, Nb and Ta, compounds with the metal-metal bond order up to 2 have been recognized.³ The triple bond, while viable on theoretical grounds, has been elusive. It was expected to occur for these metals in the oxidation state +2, but so far no Nb or Ta dimer with the d³-d³ electronic configuration and strong interactions between metal atoms has been shown to exist. In general the area of M(II) species, M = Nb or Ta, is practically unexplored and relatively few compounds are known. They include monomeric, octahedral phosphine adducts of the type MX₂L₄, where X = Cl⁴ or OAr.⁵ Recently two dinuclear Nb(II) compounds, containing η⁵-C₅H₅ and CO, have been reported but the long Nb-Nb distance of ca. 3.06 Å indicates the presence of a single bond between metal atoms.

We postulated that M(III) dimers with a double bond, spanned by a bidentate bridging ligand which would maintain the close proximity of metal atoms, had a potential for providing the desired d²-d² species upon reduction. Several such compounds have been prepared, namely, Ta₂Cl₅(O₂C-*t*-Bu)(SMe₂)(THF)₂,⁷ [Nb₂Cl₂(O₂CCH₃)₂(THT)]⁻,⁸ and M₂Cl₆(dmpm)₂,^{3c} where THT is tetrahydrothiophene and dmpm is bis(dimethylphosphino)methane. All three reacted with sodium amalgam but the products were found to be rather intractable. However, in the case of the first compound, with THT instead of SMe₂, the treatment with *t*-BuCO₂Li (intended to produce ditantalum tetracarboxylate if a Ta-Ta moiety was present) afforded after workup a small amount (10-15% based on Ta) of red crystalline material. Although its composition determined by single-crystal X-ray analysis^{9,10} was

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