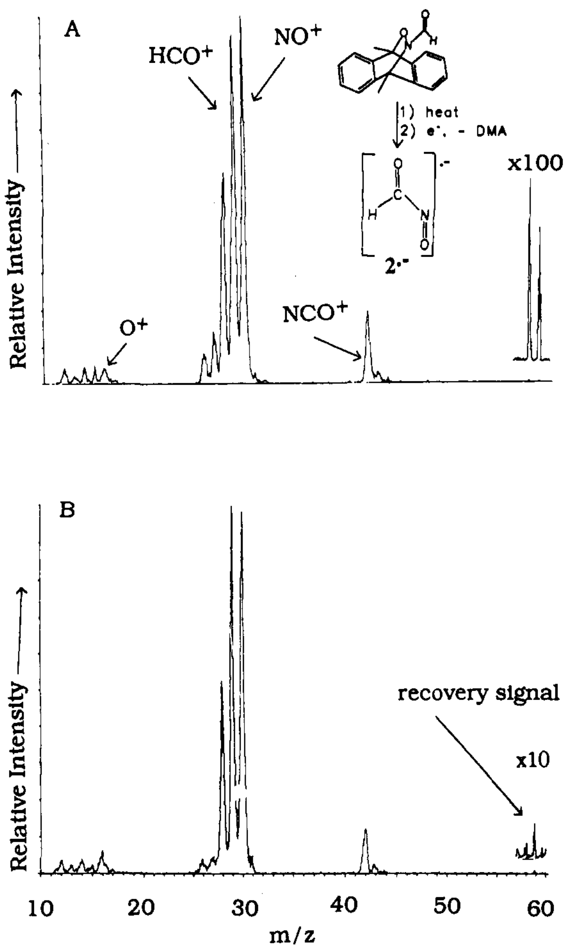

**Figure 2.** CR spectrum of $[C,H,N,O_2]^{•-}$ generated by heating the Diels–Alder adduct of nitrosoformaldehyde with 9,10-dimethylanthracene, followed by electron impact ionization in the presence of $NH_3$ (a); NR mass spectrum of $[C,H,N,O_2]^{•-}$ (b).

In the present experiment, we cannot address the multiplicity of nitrocarbene. Triplet nitrocarbene has a calculated [ROHF-(D95**)] energy of −242.438 20 au. Singlet nitrocarbene has a calculated [TCSCF(D95**)] energy of −242.434 22 au. The barrier for the rearrangement of singlet nitrocarbene to nitrosoformaldehyde is calculated to be less than 1 kcal/mol.[2] Thus, our experiments suggest that it is the triplet species of **1** which is generated in the electron detachment of $\mathbf{1}^{•-}$.[14]

Figures 2a and 2b are very similar. The abundant signal at $m/z = 29$ is most informative, since it is relatively weak in Figure 1a,b. The intense peaks at $m/z = 30$, 29, and 28 account for the bulk of the signals from this isomer. These signals are best accommodated by the nitrosoformaldehyde (**2**) structure, because simple cleavage of the CN single bond will give rise to the signals at $m/z = 30$ ($NO^+$) and 29 ($HCO^+$).

In summary, we have provided the first direct spectroscopic measurements of the neutral molecules nitrocarbene (**1**) and nitrosoformaldehyde (**2**).

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**Registry No. 1**, 19527-13-0; **2**, 5187-67-7; ethyl nitrodiazoacetate, 1572-59-4; 9,10-dihydro-9,10-dimethyl-10,9-(epoxyimino)anthracene-12-carboxaldehyde, 120290-28-0.

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(14) As suggested by a reviewer, the formation of *singlet* nitrocarbene cannot be ruled out in the electron detachment from $[HCNO_2]^{•-}$. The soformed $[HCNO_2]$ will undergo isomerization to [HC(O)NO] (**2**), followed by rapid dissociation. This sequence would also explain the decreased intensity of the reionized $NO_2^+$ signal in Figure 1b.

# A Polyoxometalate Incorporating an Organoimido Ligand: Preparation and Structure of $[Mo_5O_{18}(MoNC_6H_4CH_3)]^{2-}$

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A flourishing subdiscipline of the burgeoning field of polyoxometalate chemistry involves the derivatization of polyoxometalate frameworks by incorporation of organic and organometallic fragments.[1] The resulting species are often of interest as models for catalytic processes employing metal oxides. In conjunction with our ongoing studies directed at modeling ammoxidation chemistry,[2] we sought to prepare an imido derivative of a polyoxometalate system since imido species have been invoked as key surface intermediates in postulated ammoxidation mechanisms.[3] We report the achievement of this goal through the synthesis and X-ray structural determination of a *p*-tolylimido derivative of the $[Mo_6O_{19}]^{2-}$ system, namely, $[(n\text{-}Bu)_4N]_2[Mo_5O_{18}(MoNC_6H_4CH_3)]$ (**1**). Of particular importance is the fact that, unlike preparations of other $[(L_nM)Mo_5O_{18}]^{x-}$ systems[4,5] which rely on cluster assembly reactions, the synthesis of **1** is achieved *directly* from the hexamolybdate salt itself.

The reaction of equimolar amounts of $[(n\text{-}Bu)_4N]_2[Mo_6O_{19}]$[6] and $Ph_3P{=}Ntol$ (prepared from the reaction of *p*-tolyl azide and $Ph_3P$ in ether) in strictly anhydrous pyridine at 85 °C proceeds as shown in eq 1. Complete conversion to the bright orange tolylimido derivative is achieved within 48 h as determined by $^1H$ NMR monitoring. Separation of $Ph_3P{=}O$ is achieved by first precipitating **1** by addition of benzene, then dissolving the crude product in $CH_3CN$, and reprecipitating by addition of $Et_2O$. Crystals of **1** are readily grown by slow diffusion of $Et_2O$ into a $CH_3CN$ solution.[7] **1** is reasonably stable in air as a solid, but undergoes hydrolysis in solution to produce *p*-toluidine and the hexamolybdate salt. The IR spectrum of **1** closely resembles that of its hexamolybdate parent, except for the appearance of a strong, sharp absorption at 980 cm⁻¹; while this feature *may* derive from the molybdenum–nitrogen stretching vibration, such assignments

$$[(n\text{-}Bu)_4N]_2[Mo_6O_{19}] + Ph_3P{=}Ntol \rightarrow \underset{\mathbf{1}}{[(n\text{-}Bu)_4N]_2[Mo_5O_{18}(MoNtol)]} + Ph_3P{=}O \quad (1)$$

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(7) Anal. Calcd for $C_{39}H_{79}N_3O_{18}Mo_6$: C, 32.22; H, 5.48; N, 2.89. Found: C, 32.05; H, 5.33; N, 2.76. $^1H$ NMR ($C_5D_5N$, 23 °C): δ 7.22, 7.21, 6.95, 6.94 (AA′BB′ "quartet", $C_6H_4$, 4 H), 3.45 (m, $CH_2$, 16 H), 2.14 (s, $C_6H_4CH_3$, 3 H), 1.78 (m, $CH_2$, 16 H), 1.44 (m, $CH_2$, 16 H), 0.93 (m, $CH_3$, 24 H). $^{13}C$ NMR ($CD_3CN$, 23 °C): δ 140.1 ($C_{ipso}$), 131.3 ($C_{para}$), 130.1 ($C_{ortho}$), 126.8 ($C_{meta}$), 59.3 ($NCH_2$), 24.4 ($CH_2$), 21.3 ($C_6H_4CH_3$), 20.3 ($CH_2$), 13.9 ($CH_2CH_3$). Electronic spectrum (200–850 nm; $CH_3CN$): 348 (log ϵ = 4.3), 244 (log ϵ = 4.6), 223 (log ϵ = 4.5) nm. IR (Nujol mull): 980 (s), 959 (s), 885 (m), 790 (br, s), 590 (br, m), 440 (br, s) cm⁻¹.

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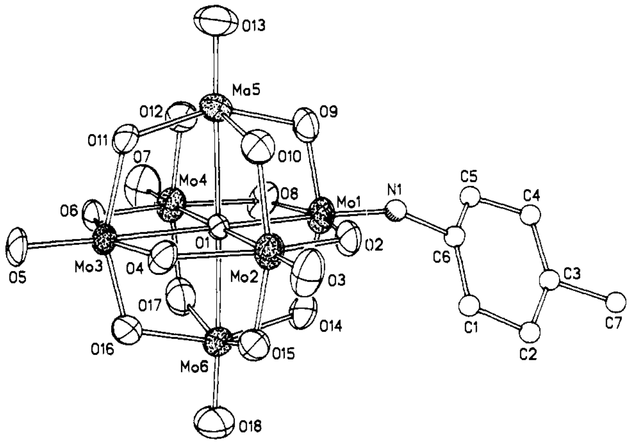

**Figure 1.** ORTEP drawing of the structure of the $[Mo_5O_{18}(MoNC_6H_4CH_3)]^{2-}$ anion. Selected bond lengths (Å) and bond angles (deg): Mo(1)–N(1) = 1.661 (18), Mo(1)–O(1) = 2.202 (11), Mo(1)–O(2) = 1.982 (12), Mo(1)–O(8) = 1.930 (11), Mo(1)–O(9) = 1.931 (12), Mo(1)–O(14) = 1.997 (12), Mo(2)–O(1) = 2.340 (10), Mo(3)–O(1) = 2.306 (11), Mo(4)–O(1) = 2.359 (10), Mo(5)–O(1) = 2.360 (9), Mo(6)–O(1) = 2.344 (9); Mo(1)–N(1)–C(6) = 154.2 (16), N(1)–Mo(1)–O(2) = 99.0 (7), N(1)–Mo(1)–O(8) = 104.6 (7), N(1)–Mo(1)–O(9) = 103.8 (7), N(1)–Mo(1)–O(14) = 99.6 (7), N(1)–Mo(1)–O(1) = 176.9 (6).

have proven to be problematic.[8] In DMF solution, cyclic voltammetry of complex **1** reveals two one-electron reductions at −0.52 V and −1.09 V (vs SCE); corresponding values for $[Mo_6O_{19}]^{2-}$ are −0.39 V and −1.12 V.

The structure of the anion of **1** is depicted in Figure 1.[9] The gross structure resembles that of its $[Mo_6O_{19}]^{2-}$ parent,[10] with a *p*-tolylimido group replacing a terminal oxo ligand. The bond lengths of the five terminal oxo ligands do not vary appreciably, ranging from 1.673 (15) to 1.700 (14) Å. The Mo(1)–O(1) distance of 2.202 (11) Å is significantly shorter than other Mo–O(1) distances, which average 2.342 (10) Å; an analogous contraction has been noted in the structure of the hydrazido(2−) system $[Mo_5O_{18}(MoNNMePh)]^{2-}$.[5a] Considerable variations are seen in the bond lengths involving the doubly bridging oxygens, which range from 1.849 (15) to 1.997 (12) Å. Klemperer[4] has correlated similar bond-length alternations in the $[(\eta^5\text{-}C_5H_5)Ti(Mo_5O_{18})]^{3-}$ anion with the $^{17}O$ NMR spectrum of that species; we will address these points in our full paper. The molybdenum–imido linkage appears to be both slightly shorter [1.661 (18) Å] and less obtuse [154.2 (16)°] than expected, but the relatively low precision of the structural data precludes a detailed analysis.

This study has demonstrated that, despite the exceedingly low surface charge density of the $[Mo_6O_{19}]^{2-}$ species,[11] direct functionalization can be accomplished in a straightforward manner under mild conditions. Our isolation of an imido derivative of a polyoxometalate system lends further credence to the proposal[3] that similar species are key surface intermediates in ammoxidation chemistry. In subsequent contributions, we will demonstrate that the reaction chemistry presented here can be extended to encompass a variety of polyoxometalate systems, including multiply substituted derivatives of **1**.

**Acknowledgment.** E.A.M. thanks the National Science Foundation for support.

**Supplementary Material Available:** Tables of atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and H atom coordinates and isotropic thermal parameters for **1** (8 pages); listing of observed and calculated structure factors for **1** (21 pages). Ordering information is given on any current masthead page.

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(9) Crystal data for $C_{39}H_{79}N_3O_{18}Mo_6$ (**1**): orange crystals, monoclinic, $P2_1/c$, $a = 12.774$ (4) Å, $b = 22.502$ (9) Å, $c = 19.716$ (7) Å, $\beta = 106.33°$, $V = 5439$ (4) Å$^3$, $Z = 4$. Of 7579 reflections collected ($T = 294$ K, $2\theta_{max} = 45°$), 3718 were independent and observed ($4\sigma F_0$). Except for C and N atoms, all non-hydrogen atoms were anisotropically refined. H atom contributions were idealized. $R = 7.48\%$ and $R_w = 8.90\%$. Disorder within the butyl and tolyl groups accounts for the high $R$ factor and distortions in these groups.

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# Activation Parameters for Triplet δ-Hydrogen Abstraction by *o*-*tert*-Butylbenzophenones: No Tunneling but an Entropy-Controlled Inductive Effect in the Isoelectronic Anilinium Ion

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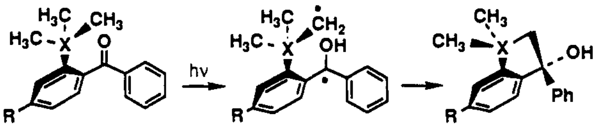
We recently reported that *o*-benzoyltrimethylanilinium ion as its $BF_4$ salt (OTMABP)[1] mimics *o*-*tert*-butylbenzophenone (OTBBP)[2] in undergoing facile photoinduced cyclization to indanol derivatives. We have now measured the activation parameters for δ-hydrogen abstraction in the triplet states of these two ketones as well as in 2,4-di-*tert*-butylbenzophenone with fully deuterated *tert*-butyl groups. We find no evidence for tunneling but do note that the inductive deceleration caused by the positive nitrogen atom in OTMABP is due entirely to a lower entropy of activation.



OTBBP : R = H, X = C OTMABP : R = H, X = N$^+$ 24tBBP : R = t-Bu, X = C

The triplet decay of OTMABP was studied as a function of temperature in methanol for comparison to the similar study done on OTBBP.[2] Triplet lifetimes were measured by monitoring decay of the T–T absorption at 625 nm following excitation of <0.01 M solutions by a nitrogen laser (337 nm). Figure 1 compares plots of log ($k_H/T$) vs $1/T$ for the two compounds. Since there are no known decay processes of triplet ketones with rate constants within an order of magnitude of the decay rates measured, we can safely assume that the only significant mode of triplet decay at all temperatures is hydrogen abstraction. The high cyclization quantum yields for both compounds[1,2] at room temperature validate this premise. Quenching studies had indicated that triplet OTMABP is only 1/30 as reactive as triplet OTBBP.[1] The flash studies verify this finding and furthermore indicate that the two compounds have identical activation energies and enthalpies, within experimental error. The factor of 30 difference in reactivity is entirely due to a more negative entropy of activation for the ketone containing the positive nitrogen.

It is commonly assumed that inductive effects on reactivity involve primarily changes in activation enthalpies. Such a situation is entirely reasonable for ionic reactions with large activation energies. However, a hydrogen atom transfer has a low activation energy and is a neutral reaction, since the reactant and product have the same charge. Nonetheless, significant inductive effects on reactivity are well-known in radical reactions and are thought to reflect charge transfer specifically in the transition state (TS).[3]

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