M NaCl hardly perturbs either a_N or W (Table I). Moreover, we have shown previously[1] that the Z value for micellar water at $R = 3.1$ lies midway between that of bulk water and methanol. Fluorescent probe data likewise indicate a rather high water polarity at low R values.[1] Thus, presently available evidence is not consistent with water pools achieving a polarity approximating that of benzene.[14]

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(5) $W = W_0[(W_1/W_0) - (W_{-1}/W_0)]$ where W_1, W_0, and W_{-1} are the peak-to-valley widths of the low, middle, and high field portions of the triplet, respectively. Values of W, which are proportional to rotational correlation times, were calculated by the "ratio of heights" method. See A. S. Waggoner, O. H. Griffith, and C. R. Christensen, *Proc. Nat. Acad. Sci. U. S. A.*, **57**, 1198 (1967).
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(15) Recipient of a Camille and Henry Dreyfus Teacher-Scholar Grant and a National Institutes of Health Research Career Development Award.

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Ammonia Formation from Molybdenum-Bound Dinitrogen under Weakly Reducing Protic Conditions

Sir:

Conversion of transition metal bound dinitrogen (N_2) to ammonia (NH_3) by means of mild reducing agents is regarded as a fundamental and challenging problem in inorganic chemistry. Past reports in the biologically relevant molybdenum area concern $^{15}NH_3$ formation from the comparatively stable *trans*-Mo($^{15}N_2$)$_2$(dppe)$_2$ (**1**)[1] when acted upon in THF by naphthalene radical anion (2.60 V)[2] or by the combination $[Fe_4S_4(SC_2H_5)_4]^{3-}$-fluoranthene radical anion (1.77 V).[3] While studying the effect of solvent on such reductions,[4] we observed that abundant amounts of $^{15}NH_3$ are generated when the complex **1** alone is merely treated with aqueous acid in *N*-methylpyrrolidone (NMP) or propylene carbonate as solvent, a reaction in which presumably the transition metal itself also acts as the reductant.

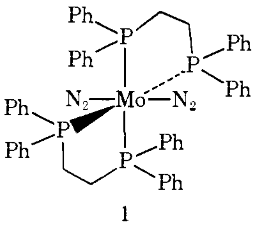

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Table I. Effect of Solvent on Reduction of Complex **1**[a]

Solvent	Acid	Concn (10^{-1} *M*)	Mol of NH_3/mol of Mo
NMP	HBr	4.5	0.286
Propylene carbonate	HBr	2.3	0.190
Triethyl phosphate	HBr	4.5	0.014
THF	HBr	4.5	0.000_9
THF	HCl	6.4	0.007_5

[a] [1] = 2.3 × 10^{-3} *M*, T = 25°, 29 hr.

Table II. Effect of Acid on Reduction of Complex **1**[a]

Acid	Concn (10^{-1} *M*)	Temp, °C	Mol of NH_3/mol of Mo
HCl	6.0	25	0.002
HCl	1.2	50	0.079
HBr	2.4	25	0.368
HBr	4.5	25	0.286
p-TSA	3.4	25	0.045
CF_3SO_3H	2.8	25	0.003

[a] [1] = 2.4–5 × 10^{-3} *M*, 29 hr.

In a typical experiment, 100 mg of complex **1**[5] was dissolved in 50 ml of NMP. After degassing with argon, 5 ml of redistilled aqueous HCl or HBr was added dropwise, and stirring was continued at 25° for ca. 30 hr. In the work-up, NH_4Cl and water were added, and the solution was rotoevaporated above room temperature nearly to dryness. The residue was taken up in water, and $^{14/15}NH_3$ was distilled under Kjeldahl conditions and trapped in aqueous HCl. The $^{15}NH_3$ content was determined by mass spectral analysis, in which procedure background $^{15}NH_3$ values were determined for NMP alone, and for complex **1** without use of mineral acid (0.003 mol of NH_3/mole of Mo).

The solvents $PO(OC_2H_5)_3$ and THF were much less efficacious for NH_3 production (Table I), while DMF and DMSO underwent serious side reactions. Hydrobromic acid was more effective than hydrochloric, trifluorsulfonic, or *p*-toluenesulfonic acid (Table II), preliminary data suggesting an optimal HBr:Mo ratio of about 100:1. Even after a few hours reaction time, the NH_3 yields were considerable. In no experiment could product hydrazine be detected (>5%) with *p*-dimethylaminobenzaldehyde. The complex $Fe^{15}N_2H_2[PC_2H_5(C_6H_5)_2]_3$[7] was found not to yield $^{15}NH_3$ under any conditions assayed. The course of the $^{15}NH_3$ producing reaction is adversely affected by impurities; for example, those present in NMP which is not freshly distilled from $NaOCH_3$, or in complex **1** prepared through use of Na sand rather than Na/Hg.

Since the N_2 complex **1** is converted to the species $MoBr_2(N_2H_2)(dppe)_2$ (**2**) under conditions[8] similar to those described herein for the generation of NH_3 from **1**, it seems reasonable that **2** mediates the latter process. In keeping with this interpretation, we found that subjection of **2** alone to reaction conditions used with **1** (as described above) resulted at least 0.15 mol of $^{15}NH_3$/mol of Mo, and that equimolar amounts of ^{15}N-labeled **2** and ^{14}N **1** gave rise to 0.48 mol of $^{15}NH_3$/mol of Mo (**1** + **2**)[9]. The high NH_3 yield in this experiment supports the intermediacy of **2** in the overall process **1** → NH_3; a second Mo may simply act as a reducing agent or may form a binuclear complex, e.g.,

$Mo_x{=}NN{=}Mo_y$, which leads to nitride as the NH_3 precursor. That Mo nitride formation precedes actual NH_3 generation is consistent with the observation that no free NH_3 is liberated when the room temperature reaction mixture is treated with excess NaOH—presumably the 100°, ca. pH 7 hydrolysis step (*vide supra*) is required for disruption of the intermediate nitride.

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(9) [^{15}N]-**2** and [^{14}N]-**1** undergo complete isotopic exchange during 1 hr in THF at 25°.

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Oxidation of Phenol to Phenoxyl Radical by O⁻ [1]

Sir:

During the course of studies of the reactions of O^- with aromatic compounds, we have had occasion to determine the rate constant for its reaction with phenoxide anion. This rate constant was found to be an order of magnitude greater than that expected for addition of O^- to aromatic rings.[2-5] Pulse radiolysis observations clearly show that the predominant product is phenoxyl radical. These facts suggest very strongly that this oxidation occurs directly via transfer of an electron from the phenoxide anion to O^-, i.e.

$$\cdot O^- + C_6H_5O^- \xrightarrow{H_2O} OH^- + C_6H_5\dot{O} \qquad (1)$$

We briefly report here the results which substantiate this suggestion.

Pulse radiolytic observations were made using the computer controlled system described by Patterson and Lilie.[6] The radical O^- was produced by irradiating 1 *M* NaOH solutions saturated with N_2O. Under these conditions essentially all (>99%) of the primary radicals are converted to O^-. The NaOH used was Baker Analyzed Reagent stated to contain <0.5% carbonate. In 1 *M* solutions of this base reactions of O^- with trace impurities contribute $\sim 2 \times 10^4$ to the overall observed rate[5] and appropriate corrections have been made for this contribution in the following rate constant determinations.

At pH 14 the absorption spectrum taken ~5 μsec after the pulse irradiation of a 10^{-3} *M* phenol solution showed the well-defined maxima at 385 and 402 nm previously observed for phenoxyl radical.[7,8] A weak band was also detected at 372 nm. The band at 402 nm is extremely sharp (band width of only 6 nm) and characteristic of phenoxyl radical. Examination of the system at pH 11, where phenoxyl radical is known to result from OH addition, shows a band of essentially identical shape and intensity. The features of the spectrum below 390 nm are also similar at the two pH values, although it is clear that the small contribution from the underlying absorption of cyclohexadienyl radical (produced by the residual H atoms) present at the lower pH is absent in the experiments at pH 14. The extinction coefficients determined at pH 14 are respectively 2900, 2300, and 1300 M^{-1} cm^{-1} at 402, 385, and 372 nm.

The reaction of O^- with the phenoxide ion was followed directly by examining the buildup of phenoxyl radical at 402 nm. The rate constant determined from the reaction periods observed over the concentration range $1\text{-}8 \times 10^{-4}$ *M* was 7.3×10^8 M^{-1} sec^{-1}. An essentially identical rate constant of 7.1×10^8 M^{-1} sec^{-1} was determined from the effect of ethanol in reducing the yield of phenoxyl radical in competitive experiments similar to those previously described[5] (the absorption of phenoxyl radical was measured at 402 nm 2-5 μsec after the pulse and $k(O^- + C_2H_5OH)$ was taken as 12.2×10^8 M^{-1} sec^{-1}). At pH 14 the contribution from OH addition to the ring should be only $\sim 5 \times 10^7$ M^{-1} sec^{-1} so that the net rate constant ascribable to reaction 1 is 6.7×10^8 M^{-1} sec^{-1}.

Known rate constants for reaction of O^- with most other aromatic systems are $<10^8$ M^{-1} sec^{-1} [2-5] so that the rate constant given above is unusually high. In order to provide comparable information on a directly related system the reaction of O^- with *p*-phenoxybenzoic acid was examined (experiments were attempted on diphenyl ether but only a limit for the rate constant could be determined because of its low solubility). No significant absorption was observed in the region of 400 nm but rather an absorption characteristic of hydroxycyclohexadienyl radicals was found at 337 nm. This absorption spectrum was, in fact, identical with that observed at pH 11.0 where OH addition is presumably quantitative (k(OH + *p*-phenoxybenzoic acid) was determined to be 7.0×10^9 M^{-1} sec^{-1}). The measured absorbances were similar at both values of pH indicating that, in 1 *M* base, addition to the ring is the predominant reaction. The rates for reaction of O^- with *p*-phenoxybenzoic acid were determined by following the growth of the absorption at 337 nm. After correcting for the partial contribution from reaction of the residual OH radicals (5×10^7 M^{-1} sec^{-1}), the results obtained in this particular study gave 1.6×10^8 M^{-1} sec^{-1} for the rate constant for reaction of O^- with *p*-phenoxybenzoic acid or a partial rate constant of 8×10^7 M^{-1} sec^{-1} per aromatic ring. This rate constant is of the magnitude expected for O^- reaction with the aromatics.

It does not appear that the high rate constant for reaction of O^- with phenoxide anion can easily be explained by a mechanism similar to that operative with OH in neutral solution where addition is followed by elimination of water.[8] There is no precedent for an addition reaction of O^- of the magnitude determined here with either aromatic or unsaturated aliphatic compounds. The studies on *p*-phenoxybenzoic acid show that the rate for addition of O^- is not increased significantly over unsubstituted aromatics by the C_6H_5O group (which has a Hammett σ parameter approaching that of O^-). We conclude, therefore, that oxidation of phenoxide anion does not take place by an addition mechanism but rather by direct transfer of an electron to O^-. The reaction is essentially quantitative and results in a very clean way of producing phenoxyl radicals for kinetic and spectroscopic studies.