

This relationship between the ketyl-5-hexenyl iodide reaction and the Wittig rearrangement of benzhydryl 5-hexenyl ether is further confirmed by the ratios **1c:2c:3c**, which are 41:5:54 for the ketyl reaction and 46:5:49 for the Wittig rearrangement, the same within experimental error. It is clear that these products result from the same process in the two reactions, collapse of cyclopentylmethyl-ketyl radical pairs. Since the cyclization of 5-hexenyl radicals is too slow ( $k \approx 10^5 \text{ sec}^{-1}$ )<sup>11</sup> to compete with cage reactions (which must occur within about  $10^{-9}$  sec),<sup>12</sup> **1c**, **2c**, and **3c** are intermolecular Wittig rearrangement products (Scheme I).

The ratios **1h:2h:3h** are 45:8:47 from the ketyl-5-hexenyl iodide reaction but 77:13:10 from the Wittig rearrangement of benzhydryl 5-hexenyl ether. Since a large fraction of the 5-hexenyl radicals escaping reaction with their geminate partners must cyclize,<sup>13</sup> **1h**, **2h**, and **3h** must be primarily intramolecular rearrangement products. Thus, the immediate product precursors must be significantly different for the intramolecular and intermolecular portions of the Wittig rearrangement.

There are three *limiting* descriptions of the intramolecular Wittig rearrangement path which incorporate factors that could be held solely responsible for the intramolecular and intermolecular product differences. (1) Radical pairs are not intermediates. (2) Radical pairs are intermediates, but their collapse to product competes effectively with mutual reorientation of the radicals, giving preferential coupling at the sites of the ketyl which are initially near the alkyl radical. (3) Radical pairs are intermediates, but different states of ion aggregation and solvation or the different initial electronic spin characters of the collapsing radical pairs for the intramolecular and intermolecular pathways give rise to different product distributions.

Possibility 1 is the least attractive limiting description of the intramolecular process. Since the fragments to which the ether anions separate at large distances are radicals, it is unreasonable to suppose that they are not radicals at separations of one or two molecular diameters. Yet, appreciable fractions of radical pairs at these smaller separations should be expected to diffuse together and react. Thus, there should be some secondary recombination<sup>12</sup> contributing to the intramolecular reaction.

Possibilities 2 and 3 are more reasonable limiting descriptions, with possibility 2 especially accounting nicely for the observed intramolecular product distribution. However, it must be recognized that a considerable fraction of the intramolecular reaction could occur through primary recombination, in which the radicals never separate by so much as a molecular diameter.<sup>12</sup> In fact, if we assume that possibility 2 obtains and that secondary recombination should give the same ratios **1h:2h:3h** as the ketyl-alkyl iodide reaction then we calculate that at least 0.8 of the intramolecular pathway must be described as primary recombination.<sup>14</sup> Since

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(13) Kinetic analysis of the reaction, using mostly known rate constants, indicates that at least 90% of the 5-hexenyl radicals escaping geminate recombination should cyclize, probably more. The concentration of ketyl in these reactions is, of course, quite low.

(14) This presumes that relative rotational relaxation of the radical partners is essentially complete between encounters.

primary recombination of radical pairs,<sup>15</sup> rearrangements through tight particle pairs describable (possibly) as radical-nonradical resonance hybrids,<sup>17</sup> and concerted migrations may all give retention of configuration of migrating groups without generating CIDNP, it is problematical whether these will be operationally distinguishable.

Occam's razor, considered in conjunction with the intermolecular rearrangement mechanism, supports a radical pair description of the intramolecular rearrangement as well, with the possibility that a substantial fraction might be considered as primary recombination of geminate radicals.

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(15) Only secondary recombination gives CIDNP.<sup>16</sup>

(16) F. J. Adrian, *J. Chem. Phys.*, **53**, 3374 (1970); **54**, 3912, 3918 (1971).

(17) H. Lemaire and R. Subra, *Ind. Chim. Belge*, **36**, 1059 (1971).

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## Molybdenum(IV) in Aqueous Solutions

Sir:

The role of molybdenum in enzymatic reactions recently aroused interest in the nature of the aquo ions of molybdenum in its various oxidation states.<sup>1,2</sup> Bowen and Taube<sup>1</sup> demonstrated the existence of the molybdenum(II) aquo ion  $\text{Mo}_2^{4+}$  and of the molybdenum(III) hexaquo ion  $\text{Mo}(\text{H}_2\text{O})_6^{3+}$ . Molybdenum(V) was recently shown to exist in aqueous solutions of noncomplexing acids as a binuclear cation of ionic charge +2, with a di- $\mu$ -oxo structure.<sup>2</sup> Whereas the existence of molybdenum aquo ions in oxidation states +2, +3, and +5 (and +6) has been established, there has been no indication, so far, of the existence of molybdenum(IV) as a stable aquo ion in solution. Except for a few complex ions of molybdenum(IV), such as the octacyano ion and its derivatives,<sup>3</sup> the chemistry of molybdenum(IV) in aqueous solution is virtually unknown. The accepted view<sup>4</sup> of this oxidation state is that molybdenum(IV) cannot exist in aqueous solution and that if it is formed as a transient intermediate during reduction of molybdenum(VI) or molybdenum(V) it would undergo rapid disproportionation to molybdenum(III) and molybdenum(V).

We wish to report the discovery of a stable aquo ion of molybdenum(IV) in aqueous solution. While investigating substitution reactions of  $\text{Mo}(\text{H}_2\text{O})_6^{3+}$ , we observed that an almost colorless solution of this ion in *p*-toluenesulfonic acid<sup>1</sup> (HPTS) acquired a pinkish tint after prolonged storage under a paraffin protective layer (used to prevent exposure to the atmosphere). Absorption of this aged solution on a cation-exchange column (Dowex 50X-2) revealed a sharp dark red band above the light yellow band of hexaaquamolybdenum-

(1) A. R. Bowen and H. Taube, *J. Amer. Chem. Soc.*, **93**, 3287 (1971).

(2) M. Ardon and A. Pernick, *Inorg. Chem.*, in press.

(3) R. B. Bucat and D. W. Watts, *MTP (Med. Tech. Publ. Co.) Int. Rev. of Sci.: Inorg. Chem., Ser. One*, **9**, 165 (1972).

(4) G. P. Haight and Alfred Katz, *Acta Chem. Scand.*, **15**, 2026 (1961); **16**, 659 (1962).

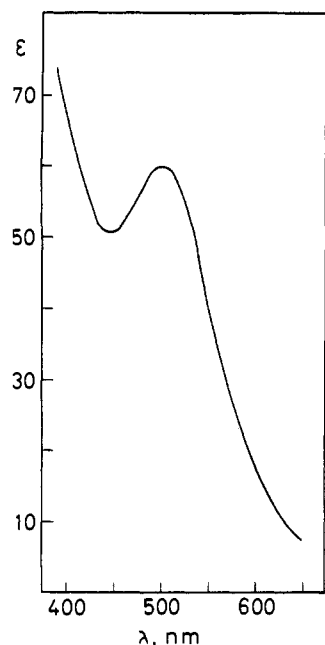


Figure 1. Visible spectrum of Mo(IV) in 1 M HPTS.

(III). The  $\text{Mo}^{3+}$  ion was eluted slowly under nitrogen, with 1 M HPTS. This eluent failed to remove the red band. A 4 M HPTS solution eluted the red band slowly, causing it to move as a single distinct band until it was removed from the column. This ion exchange behavior indicated a cation with a charge greater than +3, presumably +4.

In order to facilitate a proper investigation and identification of the red ion, a more efficient preparative procedure was developed. An equimolar mixture of 0.01 M molybdenum(III) and molybdenum(V) in 1 M HPTS (molarity given in terms of moles of Mo atoms in both oxidation states) was heated at  $90^\circ$  in an inert atmosphere for 1 hr. During this time the solution turned red. The cooled solution was absorbed on a cation-exchange column. Elution with 0.5 M HPTS removed a band of the unreacted dipositive Mo(V) ion.<sup>2</sup> This stage was followed by elution with 1 M acid in order to make sure that any unreacted  $\text{Mo}^{3+}$  is removed from the column. The red ion was finally eluted with 4 M acid as described above. The purified solution of the red ion was concentrated by repeated absorption on a short cation-exchange column followed by elution with HPTS (or  $\text{HClO}_4$ ). By this procedure solutions approximately 0.04 M in molybdenum were obtained. The visible spectrum of the red ion is given in Figure 1.

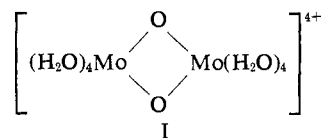
Aliquots of the red solution were titrated with a standard  $\text{KMnO}_4$  solution before and after reduction with a Jones reductor<sup>3</sup> to Mo(III). The ratio of permanganate consumed was 2:3, respectively, thus proving that the oxidation number of the red ion is +4. The result of four determinations of the oxidation number was  $+4.0 \pm 0.2$ .

The red ion was absorbed on a cation-exchange column of known capacity until all of its  $\text{H}^+$  ions were replaced by Mo(IV). After rinsing the column with water the red ion was eluted with acid and titrated with  $\text{KMnO}_4$ . The charge per Mo atom was determined by dividing the capacity of the resin by the number of

(5) I. M. Kolthoff and K. Belcher, "Volumetric Analysis," Vol. 3, Interscience, New York, N. Y., 1957, p 92.

moles of Mo atoms eluted from it. A charge of  $+2.0 \pm 0.1$  per molybdenum atom was obtained (average of three determinations).

Since the ion-exchange behavior of the red ion indicates a charge of +4 and since the charge per Mo atom is +2, it is concluded that the red ion is binuclear. The most probable structure of the ion is I. The di- $\mu$ -



oxo bridge to the Mo atoms is well-known in Mo(V) compounds<sup>2,6</sup> as well as in some salts of Mo(III).<sup>7</sup> An alternative structure with a Mo-Mo bond and two terminal oxygen atoms is much less probable.

The most striking property of the ion is its remarkable stability to air oxidation. In acid solution above 1 M, the concentration of Mo(IV) decreases very slowly if the solution is exposed to the atmosphere. The red color of the exposed solutions persists for many days.

The second unexpected property is the resistance of the ion to disproportionation. Even at  $90^\circ$  the ion is quite stable in an inert atmosphere. It should, however, not be concluded from our preparative procedure that molybdenum(IV) is more stable thermodynamically than the mixture of molybdenum(III) and molybdenum(V). Molybdenum(V) is not completely consumed by the formation reaction of molybdenum(IV) and can be recovered by ion-exchange chromatography. It may be that Mo(IV) is formed by the reduction of solvent water by Mo(III), with Mo(V) acting as a catalyst. The mechanism of the formation reaction of Mo(IV) (in the process described above) is now being investigated, as are other oxidation reactions of  $\text{Mo}^{3+}$  that produce the  $\text{Mo}_2\text{O}_2^{4+}$  ion. We are also investigating the oxidation of  $\text{Mo}_2\text{O}_2^{4+}$  by several one-electron and two-electron oxidizing agents such as  $\text{Fe}^{3+}$ ,  $\text{Ce}^{4+}$ , and  $\text{Tl}^{3+}$ .

It is hoped that the discovery of a stable quadrivalent oxidation state of molybdenum in aqueous solution may help to elucidate the mechanism of enzymatic reactions involving molybdenum.

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(7) P. C. H. Mitchel and R. D. Scarle, *J. Chem. Soc., Dalton Trans.*, 1809 (1972).

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### Iminoyl Free Radicals. An Electron Spin Resonance Identification of a New Class of $\sigma$ Radicals<sup>1</sup>

Sir:

Although there are numerous reports in the literature of organic  $\pi$  radicals only a relatively few  $\sigma$  radicals have been identified.<sup>2</sup> A free radical is considered a

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(2) For a fairly detailed listing of references to both experimental and theoretical studies on  $\sigma$  radicals, see P. J. Krusic and T. A. Rettig, *J. Amer. Chem. Soc.*, **92**, 722 (1970).