Catalysis to the Disfavored Product: The Case of $(\eta^5\text{-}C_5H_5)Mo(CO)_3^\bullet$

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Summary: The title compound is a 17e organometallic radical, which ordinarily recombines to the dimer in many solvents, including acetonitrile. In the presence of $1,4\text{-}(Me_2N)_2C_6H_4$ *(TMPD), however, the radical disproportionates to* $(\eta^5\text{-}C_5H_5)Mo(CO)_3^-$ *and* $(\eta^5\text{-}C_5H_5)Mo(CO)_3NCCH_3^+$*. The mechanism involves the radical oxidizing TMPD and reducing* $TMPD^{\bullet+}$*, whose buildup and decay were directly monitored.*

Catalytic reactions that enhance the formation of thermodynamically less favored products may provide a better route to known chemicals, or they may lead to the preparation of novel compounds. On finding a new and specific example of this phenomenon, we undertook this study not only to explore the synthetic aspects but even more to learn how the catalyst diverts the reagents from their ordinary (and diffusion-controlled) course. We have discovered a catalyst that converts an organometallic substrate to products that are less favored than that formed spontaneously.

The substrate is $(C_5H_5)Mo(CO)_3^\bullet$, or $Mo^\bullet$ for short, a 17e metal-centered radical formed by photohomolysis of the Mo–Mo bond of $(C_5H_5)_2Mo_2(CO)_6$ (or Mo_2), to which it ordinarily returns (eq 1).[1–4] In the presence of $1,4\text{-}(Me_2N)_2C_6H_4$ (tetramethylphenylenediamine, abbreviated as TMPD), a significant part of the $Mo^\bullet$ disproportionates (eq 2). The equilibrium constants[5] are $K_1 = 1.3 \times 10^{16}$ and $K_2 = 1.9 \times 10^7$. Clearly, disproportionation is the disfavored alternative; the actual product ratio is determined by the initial concentration of $Mo^\bullet$ and the catalyst concentration, neither reaction being thermally reversible.

$$2(C_5H_5)Mo(CO)_3^\bullet \xrightarrow{k_1} [(C_5H_5)Mo(CO)_3]_2 \qquad (1)$$

$$2(C_5H_5)Mo(CO)_3^\bullet + CH_3CN \xrightarrow{\text{cat. TMPD}} (C_5H_5)Mo(CO)_3NCCH_3^+ + (C_5H_5)Mo(CO)_3^- \qquad (2)$$

The flash photolysis experiment[6] allowed the independent monitoring of $TMPD^{\bullet+}$ ($\lambda_{max} = 613$ nm, $\epsilon = 1.2 \times 10^4$ L mol^{-1} cm^{-1}), the oxidized form of the catalyst. Our measurements utilized the specified reagents[7] and were carried out in anaerobic acetonitrile. We conclude that the catalytic process consists of two electron-transfer steps in succession:

$$Mo^\bullet + TMPD \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} Mo^- + TMPD^{\bullet+} \qquad (3)$$

$$Mo^\bullet + TMPD^{\bullet+} \xrightarrow{k_4(+CH_3CN)} MoNCCH_3^+ + TMPD \qquad (4)$$

The qualitative evidence we present in support of this scheme is as follows. (1) Reactions 3 and 4 are thermodynamically permissible:[5] $K_3 = 9 \times 10^{-5}$ (which lies sufficiently close to unity to allow for both directions of reaction), and $K_4 \approx 2 \times 10^{11}$. (2) $TMPD^{\bullet+}$ was formed in the period during which $Mo^\bullet$ disappeared, typically some 5–50 μs. (3) $TMPD^{\bullet+}$ is always lost completely in about 0.5–2 ms. (4) At higher concentrations of $Mo^\bullet$ and TMPD, the decay of $TMPD^{\bullet+}$ became faster and faster with each laser flash, because of the accumulation of the previously formed Mo^-. (5) $TMPD^{\bullet+}$ is stable more or less indefinitely in acetonitrile and showed no thermal reaction with $MoNCCH_3^+$ or Mo_2.[8] (6) $TMPD^{\bullet+}$ reacts with independently prepared Mo^- immediately upon mixing. (7) $TMPD^{\bullet+}$ reacts with $Mo^\bullet$, and the products are TMPD and $MoNCCH_3^+$ (an 18e species with one coordinated CH_3CN). This molybdenum cation was identified by IR in the carbonyl stretching region. (8) Less $TMPD^{\bullet+}$ was formed when Mo^- was present at the outset, and the disappearance of $TMPD^{\bullet+}$ was faster. With sufficient Mo^-, no $TMPD^{\bullet+}$ could be detected. (9) Addition of $MoNCCH_3^+$ was without effect. (10) The ionic products, Mo^- and $MoNCCH_3^+$, although thermodynamically capable of combining to the dimer, did not do so to any measurable extent even on long standing.

Several rate constants contribute to the growth and decay of $TMPD^{\bullet+}$. The family of differential equations for reactions 1, 3, and 4 have no closed-form solution, and

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(5) Pugh, J. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1992,** *114,* 3784. In this report these E^0 values (V vs SSCE) are pertinent: $MoNCCH_3^+ + e^- = Mo^\bullet + CH_3CN$, −0.51; $Mo^\bullet + e^- = Mo^-$, −0.08. Also, $TMPD^{\bullet+}/TMPD$ has $E^0 \approx 0.16$ V. Note that $Mo^\bullet$ is a better oxidant than $MoNCCH_3^+$ by 0.43 V; that is, $Mo^\bullet$ is oxidized much more easily than Mo^-. In a qualitative sense the relative values of k_{-4} $(=k_4/K_4)$ and k_3 are in accord with this, although one should not expect too much from this approach in that the reactions represented by k_4 and k_{-3} are at or near the diffusion-controlled limit.

(6) The Mo_2-containing solutions were subjected to a 0.6-μs flash from a flashlamp-pumped dye laser described previously: Melton, J. D.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1986,** *25,* 4104. Hoselton, M. A.; Lin, C.-T.; Schwartz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1978,** *100,* 2383. All the experiments used LD 490 dye.

(7) $TMPD^{\bullet+}$ was prepared by the reaction of TMPD and $AgCF_3SO_3$. $MoNCCH_3^+$ was prepared as described in: Inkrott, K.; Goetze, R.; Shore, S. G. *J. Organomet. Chem.* **1978,** *154,* 337. Mo^- was prepared as described in ref 5.

(8) The first step is unlikely to proceed through $[CpMo(CO)_3TMPD]^{\bullet+}$ (a 19e radical), since the binding constant between metal radicals and other amines is quite small.[4] Also, such an interaction would not serve to stabilize the products, which show no tendency to associate.

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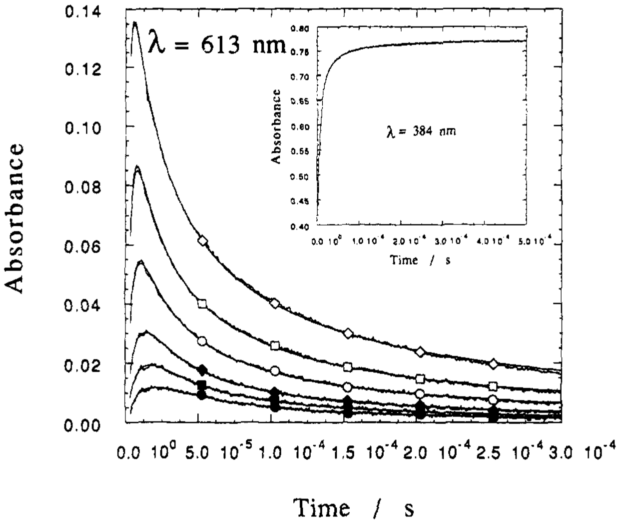

Figure 1. Measured and fitted curves showing the buildup and decay of $TMPD^{\bullet+}$ at different initial TMPD concentrations and $[Mo_2]_0$ = 50.7 μM. The values of $[TMPD]_0$, from top to bottom, are 10.0, 5.00, 2.50, 1.00, 0.50, and 0.25 mM. Inset: Measured and fitted curves for the recovery of Mo_2 in the absence of TMPD, with $[Mo^\bullet]_0$ = 74.5 μM.

so numerical methods were used. The program ZITA[9] simultaneously considers all the experiments globally[10] and so includes all the relevant starting concentrations in each separate experiment. The observed and calculated kinetic curves are shown in Figure 1. The best-fit rate constants, with k_1 fixed at its independently known value of $[2.16(3)] \times 10^9$ L mol^{-1} s^{-1} (obtained by monitoring the buildup of Mo_2 at λ_{max} = 384 nm, $\epsilon = 1.7 \times 10^4$ L mol^{-1} cm^{-1}), are $k_3 = [1.5(2)] \times 10^7$ L mol^{-1} s^{-1}, $k_{-3} = [7.9(6)] \times 10^9$ L mol^{-1} s^{-1}, and $k_4 = [1.8(2)] \times 10^8$ L mol^{-1} s^{-1} at 23 ± 2 °C.

A representative concentration–time profile is displayed in Figure 2. The changes displayed are instructive of the course of events. This catalyst opened a pathway for the organometallic radical with a kinetic barrier inherently higher than that for the ordinary pathway; that is, $\Delta G_1^\ddagger$ (4.7 kcal) < $\Delta G_3^\ddagger$ (7.6 kcal). The concentration of TMPD allows reaction 3 to occur despite this, since the actual reaction rates rather than the rate constants are the relevant quantity. As it happens, ΔG_1^0 (−22 kcal) < ΔG_2^0 (−11 kcal) < ΔG_3^0 (+4.2 kcal). The new products are less preferred than those formed when the catalyst is absent.

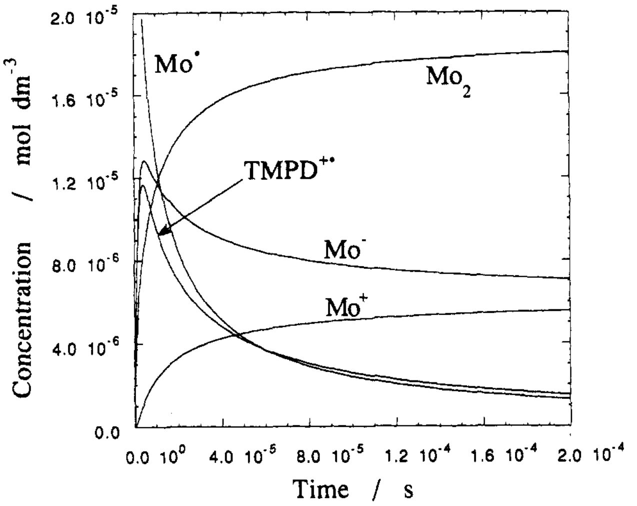

Figure 2. Simulated concentration changes at $[Mo^\bullet]_0$ = 50.0 μM and $[TMPD]_0$ = 10.0 mM.

We also observed the same behavior in the $(C_5H_5)W(CO)_3^\bullet$–TMPD system.

This scheme for electron-transfer-catalyzed disproportionation is clearly distinct from ligand-induced disproportionation,[11] although both consist of electron-transfer steps. In the scheme presented here, however, neither transition state contains a pair of molybdenums and neither reactant is a 19e metal radical.

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[9] Peintler, G. ZITA, A Comprehensive Program Package for Fitting Parameters of Chemical Reaction Mechanism, Version 3.1: Institute of Physical Chemistry, JATE: Szeged, Hungary, 1992. The first use of this program was described by: Peintler, G.; Nagypal, I.; Epstein, I. R. *J. Phys. Chem.* **1990**, *94*, 2954.

[10] That is to say, all of the kinetic curves were incorporated into a single calculation, based on those depicted in Figure 1 with varying $[TMPD]_0$ and others (not shown) where $[Mo^\bullet]$ was varied.

[11] (a) Stiegman, A. E.; Tyler, D. R. *Comments Inorg. Chem.* **1986**, *5*, 215. (b) Scott, S. L.; Espenson, J. H.; Chen, W. J. *Organometallics* **1993**, *12*, 4077.