abundance of $^{13}C$ nucleus is only 1.1%, any possible spectral interference from $^{13}C$ natural abundance signal of DNA, as shown in Figure 1B, can be greatly reduced (Figure 1C). Furthermore, this method also permits us to detect the modification at an early stage or reduce the amount of modifying agent, which may be critical since a biological event often takes place after exposure to a limited amount of active agent. Figure 1C distinctly displays four methyl carbon signals at 30.5, 36.0, 38.0 and 52.9 ppm, whose resonance designations as shown in Figure 1C can be determined on the basis of model studies of 31 different methylated nucleosides and nucleotides prepared in our laboratory. The product distribution can be determined from the integration curve.[12,22] The degree of modification may be calculated from the measurement of radioactivity by using [*methyl*-$^{14}C$]MeMS and [*methyl*-$^{13}C$]MeMS concurrently.

The observed line widths for salmon sperm DNA are approximately one-half of those for double-stranded calf thymus DNA of ~140 base pairs isolated from enzymatic degradation of chromatin.[20] The $^{13}C$ line widths and solubility in water indicates that this DNA is relatively small.[23] To study the tertiary structure effect on the chemical modification of DNA, we further modified the native salmon testes DNA[23] with [*methyl*-$^{13}C$]MeMS. Its $^{13}C$ spectrum is shown in Figure 1D. Comparison of Figure 1C,D indicates that the relative product distributions are quite different. The most remarkable difference is that the peak at 52.9 ppm corresponding to phosphomethyl signal is absent in the spectrum of alkylated salmon testes DNA. These results suggested that only the terminal phosphate group of polynucleotide can be significantly methylated. In order to test this suggestion, we treated 1.2 mm of salmon sperm DNA in 5 mL of 0.1 M Tris buffer (pH 8) with 90 units of *E. coli* alkaline phosphatase (Sigma Chemical Co.) for 1 h at 37 °C and then reacted it with [*methyl*-$^{13}C$]MeMS. The $^{13}C$ spectrum (Figure 1E) and $^{31}P$ NMR spectra[24] (Figure 2) unambiguously confirm this suggestion, since the enzyme treated DNA no longer has terminal phosphate groups, and indeed no phosphate alkylation is observed.

The approach outlined here provides a useful method for the direct study of the chemical modification of nucleic acids. Because this method avoids tedious and sometimes complicating degradative reactions of alkylated DNA, it should provide an important new approach to the determination of the sites of alkylation and mechanism of action of mutagens, carcinogens,[25-28] and anticancer agents.[29-31]

**Acknowledgment.** We gratefully acknowledge financial support from the National Cancer Institute (Grant number CA22987). We also acknowledge helpful discussions with Heinz G. Floss and technical assistance from John Kozlowski. $^{31}P$ NMR spectrum of methylated DNA was obtained from the Biomedical Magnetic Resonance Facility (National Institutes of Health, RR01077) at Purdue University.

(22) The product distributions are significantly different from previous ones determined by indirect methods (see review by: Singer, B. *Prog. Nucl. Acid Res. Mol. Biol.* **1975**, *14*, 219). However most results from other groups were obtained under different conditions (source of DNA, buffer solutions, pH values, temperature, ratio of alkylating agent to DNA). It may not be appropriate to make direct comparison and elaboration on their difference at this moment.

(23) The molar percentages of four major nucleosides of salmon sperm and salmon testes DNAs were determined by reverse-phase high-pressure liquid chromatography. They are compatible with the literature values (Kuo, K. C.; McCune, R. A.; Gehrke, C. W.; Midgett, R.; Ehrlich, M. *Nucl. Acids Res.* **1980**, *8*, 4763-4776). The percentages of double helical character were measured by digesting with $S_1$ endonuclease from *Aspergillus oryzae* (Sigma Chemical Co.) to cleave single-stranded DNA (Vogt, V. M. *Eur. J. Biochem.* **1973**, *33*, 192-200) and then separated on hydroxylapatite column to isolate double-stranded DNA (Miyazawa, Y.; Thomas, C. A. *J. Mol. Biol.* **1965**, *11*, 223-237). The molecular weight was determined by comparing with DNA molecular weight markers [hydrolysate of λ-DNA with restriction endonuclease Hind III (Boeringer Mannheim)] in the agarose electrophoresis (Philippsen, P.; Kramer, R. A.; Davis, R. W. **1978**, *123*, 371-386. Peacock, A. C.; Dingman, C. W. *Biochemistry* **1967**, *6*, 1818-1827).

| | salmon sperm DNA | salmon testes DNA |
|---|---|---|
| dA | 26.2 | 29.4 |
| dG | 20.3 | 22.0 |
| dT | 30.7 | 27.9 |
| dC | 22.8 | 20.6 |
| % double strandedness | 22 | 65 |
| $M_r$ | 92 000 | $7.4 \times 10^6$ |

(24) A detailed report on the $^{31}P$ NMR of modified nucleic acids will be published elsewhere. From Figure 2A,B, the most downfield peak at -2.8 ppm from trimethyl phosphate could be assigned to the terminal phosphate group. Methylation of this phosphomonoester caused it to overlap with one of the phosphodiester signals at -3.8 ppm (Figure 2C). (Davanloo, P.; Armitage, I. M.; Crothers, D. M., *Biopolymers* **1979**, *18*, 663-680). All signals from -3.8 to -5.0 ppm were ascribed to the $^{31}P$ resonance of random coil polynucleotide (Mariam, Y. H.; Wilson, W. D.; *Biochem. Biophys. Res. Commun.* **1979**, *88*, 861-866).

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## The Transition-Metal Nitro-Nitrosyl Redox Couple: Catalytic Oxidation of Olefins to Ketones

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Catalytic air oxidation is the method of choice for the industrial synthesis of a wide variety of chemicals. A new approach to this problem employs the transition-metal nitro-nitrosyl redox couple:

$$\text{M-NO}_2 + \text{L} \rightarrow \text{M-NO} + \text{L-O} \quad (1)$$

$$\text{M-NO} + {}^1/_2\text{O}_2 \rightarrow \text{M-NO}_2 \quad (2)$$

$$\text{L} + {}^1/_2\text{O}_2 \rightarrow \text{L-O}$$

While examples of reaction 1 have been known since at least 1962[1] and examples of reaction 2 since 1970,[2] a catalytic system that exhibits both reactions 1 and 2 was not reported until 1976.[3] The metal nitro-nitrosyl redox couple has been applied to the catalytic oxidation of CO to $CO_2$[3] and phosphines to phosphine oxides.[4] We report here a new nitro-nitrosyl redox couple based on the readily prepared complex bis(acetonitrile)chloronitropalladium(II) which catalytically air oxidizes olefins to ketones. Mechanistic evidence presented includes $^{18}O$ labeling data, spectroscopic data for intermediates, and the effect of olefin substituents. While this work was in progress, workers at Allied Chemical reported[5] that nitrosyltetraphenylporphyrincobalt is also a catalyst for the air oxidation of olefins to ketones; however, a Pd(II) cocatalyst was required and mechanistic data were limited.

*trans*-Bis(acetonitrile)dichloropalladium(II),[6] a common precursor for palladium(II)-olefin complexes,[6b,7] was treated with 1 or 2 mol of silver nitrite in acetonitrile to give quantitative yields

(1) Booth, G.; Chatt, J. *J. Chem. Soc.* **1962**, 2099-2106.
(2) Ishiyama, T.; Matsumura, T. *Annu. Rep. Radiat. Cent. Osaka Prefect.* **1970**, *11*, 50-52. (*Chem. Abstr.* **1972**, *76*, 30252v).
(3) Ugo, R.; Bhaduri, S.; Johnson, B. F. G.; Khair, A.; Pickard, A. *J. Chem. Soc., Chem. Commun.* **1976**, 694-5.
(4) Tovrog, B. S.; Diamond, S. E.; Mares, F. *J Am. Chem. Soc.* **1979**, *101*, 270-272.
(5) Tovrog, B. S.; Mares, F.; Diamond, S. E. *J. Am. Chem. Soc.* **1980**, *102*, 6616-6618.
(6) (a) Walton, R. A. *Spectrochim. Acta* **1965**, *21*, 1795-1801; Walton, R. A. *Can. J. Chem.* **1968**, *46*, 2347-2352. (b) Hegedus, L. S.; Williams, R. E.; McGuire, M. A.; Hayashi, T. *J. Am. Chem. Soc.* **1980**, *102*, 4973-4979. (c) Wayland, B. B.; Schramm, R. F. *Inorg. Chem.* **1969**, *8*, 971-976.
(7) See also the benzonitrile analogue: Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882-884.

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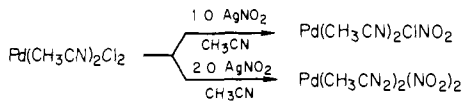
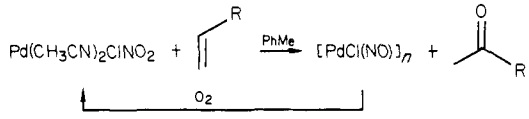
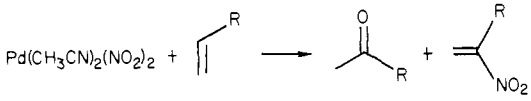
Scheme I




Scheme II




Scheme III




| | | | |
|---|---|---|---|
| PhMe | 1 | : | 11 |
| $Me_2CO$ | 7 | : | 1 |

of the new nitro complexes bis(acetonitrile)chloronitropalladium(II) (**1**)[8,9] and bis(acetonitrile)dinitropalladium(II) (**2**),[10] respectively (Scheme I). Under nitrogen at room temperature, toluene solutions of chloronitro complex **1** cleanly and selectively oxidize 1-decene to 2-decanone in 95% GC yield[8,11] based on palladium over a 15-h period (Scheme II). The major inorganic product (65% isolated yield) is a red-brown precipitate identified as $[PdCl(NO)]_n$ (**3**).[12]

In contrast, when the same reaction is carried out in air at room temperature, the yellow solution remains homogeneous at all times and the GC yield of 2-decanone reaches 235% ± 10% based on palladium. When the reaction is conducted at 60 °C in air, a brown precipitate forms (presumably $[PdCl(NO)]_n$) which later redissolves, ultimately leading to a 375% yield of 2-decanone. Decomposition of the active catalyst results in the eventual formation of the allyl chloro dimer $[(H_2CCHCHC_7H_{15})PdCl]_2$.[13]

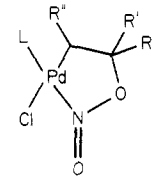
As must be the case for a catalytic cycle based on a nitro–nitrosyl redox couple, the corresponding nitrosyl complex can also be used as the catalyst precursor. Thus, reaction of a toluene suspension of $[PdCl(NO)]_n$ with 1-decene at 60 °C in air gave a 334% yield of 2-decanone. Furthermore, treatment of a toluene suspension of nitrosyl complex **3** with 28 equiv of acetonitrile in the presence of air leads to the reformation of chloronitro complex **1** in 47% isolated yield (Scheme II).

The reacton is quite general. NMR and/or GC results show qualitatively that **1** reacts with ethylene to give acetaldehyde, with propylene to give acetone (645%), with ethyl vinyl ether to give ethyl acetate, slowly with *cis*-2-butene to give 2-butanone (plus *trans*-2-butene), and slowly with *cis*-2-octene to give a number of products (presumably octanone isomers).

Treatment of 1-decene with a toluene suspension of dinitro complex **2** at room temperature leads to 2-decanone formation (9% GC yield); but the major product (101% GC yield) of the 3-week reaction is 2-nitro-1-decene[14] (Scheme III). The product selectivity can be reversed and the reaction rate greatly enhanced by employing acetone as the solvent in which case the yields of 2-decanone and 2-nitro-1-decene are 95% and 13%, respectively. The formation of nitrodecene might be related to the formation of chloroolefins in a related system.[15] This may be a useful synthetic method for the preparation of 2-nitro-1-alkenes.[16]

Although a detailed mechanism for these metal–nitro complex oxidations has not been established, some experimental data are available. Quantitative infrared spectra show that 69% $^{18}O$ enriched $Pd(CH_3CN)_2ClNO_2$ reacts with 1-decene in toluene under nitrogen to give $^{18}O$ labeled 2-decanone with no detectable (<5%) dilution of the isotopic label.[8] This is the first definitive proof that olefin oxidation by a transition-metal–nitro complex involes oxygen transfer from the nitro group to the olefin.[17]

At least two intermediates can be observed in the reaction of chloronitro complex **1** with olefins. Addition of most olefins to a solution of **1** in a noncoordinating solvent produces an instantaneous color change from orange to yellow. IR and NMR spectra[18] are consistent with the displacement of acetonitrile from the palladium accompanied by rapid, reversible coordination of the olefin. In coordinating solvents or with electron-deficient olefins, the color change is not observed and the reaction rate is greated reduced. Over a period of 1-20 min, a second species is generally formed. Spectral data and lifetimes for this species[19] are consistent with metallocycle i:




i

The present system is the first for which spectroscopic evidence has been obtained for an intermediate involved in oxygen-atom transfer by a nitro group. All previous suggestions were based solely on mechanistic considerations.[5,17,20] We attribute the relative stability of proposed intermediate i to the favorable five-membered ring size (vs. four for CO[17] and NO[20]) and the inhibition of $\beta$-hydrogen elimination in the metallocycle[21] (vs. open chain[5]).

The formation of methyl ketones in preference to aldehydes is consistent with the absence of detectable concentrations of any intermediate having $R'' \neq H$ and literature concerning the regioselectivity of nucleophilic attack on olefins complexed to palladium(II).[6b,22] A number of detailed mechanisms can be postulated for the conversion of the intermediate to ketone product,[23] but all require net hydride transfer from the carbon

(8) Experimental details for most syntheses and reactions reported here are available as supplementary material.

(9) IR (KBr) 2989 (vw), 2920 (vw), 2325 (w), 2296 (vw), 2252 (vw), 1597 (w), 1409 (s), 1391 (sh), 1336 (s), 836 (m), 607 (vw), 559 (w) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.19 (s); mp 107–109 °C dec; Anal. ($C_4H_6ClN_3O_2Pd$) C, H, Cl, N.

(10) IR (KBr) 2995 (vw), 2934 (w), 2326 (w), 2297 (w), 2253 (vw), 1630 (br, w), 1406 (s), 1388 (s), 1347 (s), 837 (m), 607 (w). Anal. Calcd for $C_4H_6N_4O_4Pd$ C, 17.13; H, 2.16; Cl, 0.00; N, 19.97. Found: C, 16.74; H, 2.17; Cl, 0.56; N, 18.20. (Partial decomposition occurred on attempted recrystallization).

(11) Reaction aliquots were quenched with triethylamine prior to GC analysis.[8] The validity of the quenching procedure was confirmed by quantitative IR measurements of the C=O stretch of 2-decanone.

(12) Smidt, J.; Jira, R. *Chem. Ber.* **1960**, *93*, 162–5.

(13) $^1H$ NMR ($CCl_4$) $\delta$ 5.40 (1 H, d of d of d, $J$ = 12, 12, 7 Hz), 4.1–3.5 (1 H, br m), 3.89 (1 H, d, $J$ = 7 Hz), 2.86 (1 H, d, $J$ = 12 Hz), 1.9–1.4 (2 H, s), 1.6–1.1 (10 H, br s), 0.90 (3 H, br t). With propylene the product is $[(C_3H_5)PdCl]_2$, identified by comparison with an authentic sample.

(14) IR ($CCl_4$) 2956, 2929, 2857, 1531 (s), 1468 (w), 1432 (w), 1344, 937 $cm^{-1}$; $^1H$ NMR ($CCl_4$) $\delta$ 6.39 (1 H, s), 5.52 (1 H, s), 2.61 (2 H, t, $J$ = 7 Hz), 1.8–1.1 (12 H, br s), 0.91 (3 H, br t). Anal. ($C_{10}H_{19}NO_2$) C, H, N.

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(17) An $^{18}O$ labeling experiment has been carried out for CO oxidation by a nitronickel complex: Doughty, D. T.; Gordon, G.; Stewart, R. P., Jr., *J. Am. Chem. Soc.* **1979**, *101*, 2645–2648.

(18) For propylene + **1** in $CDCl_3$, $\nu_{C=C}$ 1540 $cm^{-1}$; $^1H$ NMR time averaged peaks due to propylene are down field and the peak due to acetonitrile upfield of their free and coordinated values, respectively.

(19) For propylene + **1** in $CDCl_3$ after 20 min (R' = R'' = H; R = $CH_3$): $^1H$ NMR $\delta$ 4.55 (1 H, ~sextet, $J \sim 6$ Hz), 3.48 (1 H, d of d, $J$ = 4.7, 8.8 Hz), 3.16 (1 H, d of d, $J$ = 6.5, 8.8 Hz), 1.56 (3 H, d, $J$ = 6.3 Hz); IR $\nu_{N=O}$ 1628 $cm^{-1}$. This intermediate is detectable for at least 1 h at 25 °C.

(20) Ileperuma, O. A.; Feltham, R. D. *Inorg. Chem.* **1974**, *16*, 1876–1883.

(21) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4451–4452.

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(23) 1-Decene oxide and decanal are not isomerized under the reaction conditions.

$\beta$ to palladium to the carbon $\alpha$ to palladium. An intermediate lacking a $\beta$ hydrogen, formed from **1** and isobutylene with R = R′ = $CH_3$ and R″ = H,[24] decomposes by a different pathway to yield an allyl complex with no evidence for the expected olefin oxidation products, isobutyraldehyde or 2-butanone.

**Acknowledgment.** This research was carried out at Brookhaven National Laboratory under contract with the U. S. Department of Energy and supported by its Office of Basic Energy Sciences.

**Supplementary Material Available:** Experimental details for syntheses and reactions (5 pages). Ordering information is given on any current masthead page.

(24) $^1H$ NMR ($CDCl_3$) $\delta$ 3.32 (2 H, s), 1.74 (6 H, s); NMR yield ~60% based on Pd; IR ($CDCl_3$) $\nu_{N=O}$ 1620 $cm^{-1}$.

## Thermochemistry and Unimolecular Reactions of Ionized 1,2-Dimesityl-2-phenylethanone and 2,2-Dimesityl-1-phenylethanone and Their Enols and Enol Acetates in the Gas Phase

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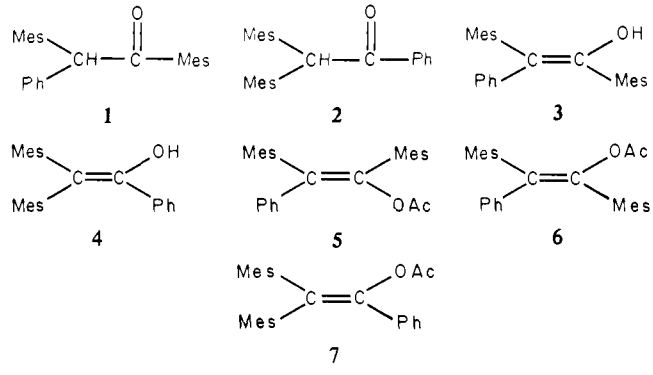
Keto–enol tautomerism of gas-phase ions is a subject of intense current research activity.[1] In all of the reports published to date, one of the tautomers, usually the enol, was produced as a fragment ion by dissociative ionization rather than as a parent ion by direct ionization. The most common route to enol production in the gas phase has been the McLafferty rearrangement reaction. Following Fuson[2a,b] we synthesized the isomeric ketones 1,2-dimesityl-2-phenylethanone (**1**) and 2,2-dimesityl-1-phenylethanone (**2**) and their stable isomeric enols *Z*-**3** and **4** as well as the *E*- and *Z*-enol acetates **5** and **6**[2a] and the enol acetate **7**[2b] and determined their geometric structures.[2c,d] For the first time this enables (i) ionization of both enol and keto forms directly in the gas phase, thus obtaining the relative heats of formation of the ions, and observation of their unimolecular reactions; (ii) comparison of the behavior of the ionized enols formed by cleavage of the acetate esters, with that of the directly ionized enol and ketone forms.

Table I. Equilibrium Data, Ionization Potentials, and $T_{1/2}$ Values for the Reactions of 1-7

| compd | IP, eV | $T_{1/2}$, meV (transition) | $\Delta G°$, kcal $mol^{-1}$ (process) |
|---|---|---|---|
| 1 | 8.1 ± 0.2 | 12.6 (356 → 147) | 0.6,[a] 1.12[b] (1 ⇌ 3) |
| 3 | 7.5 ± 0.2 | 34.5 (356 → 147) | 0.57[a] (1 ⇌ 3) |
| | | | 1.06[b] |
| 2 | 7.6 ± 0.1 | 20.6 (356 → 105) | −0.5 ± 0.1[a] (2 ⇌ 4) |
| | | 24.7 (356 → 251) | −1.12[b] |
| 4 | 7.5 ± 0.1 | 33.3 ± 3 (356 → 105) | −0.51 ± 0.13[a] (2 ⇌ 4) |
| | | 37.3 (356 → 251) | −0.93[b] |
| 5 | | 33.4 ± 2.0 (356 → 147) | |
| 6 | | 35.3 ± 0.1 (356 → 147) | |
| 7 | | 33 ± 3 (356 → 105) | |
| | | 37.0 (356 → 251) | |

[a] In hexane at 335 K. [b] In PhCl at 405 K.




Mes = 2,4,6-$Me_3C_6H_2$

Metastable ion dissociations were studied on a Varian MAT 311 instrument (reverse Nier–Johnson geometry) by scanning the accelerating voltage. Scans were carried out automatically and accumulated with the aid of a D116 Digital Computer Controls minicomputer. Ionization potentials were determined by the semilogarithmic method[3] using benzene (IP = 9.5 eV) and argon (IP = 15.8 eV) as reference standards, on a Varian MAT 711. The results are given in Table I.

In order to evaluate the contribution of the neutral species to the $\Delta H_f$ difference of the ions, the two ketone–enol pairs were equilibrated in hexane and chlorobenzene in the presence of $CF_3COOH$. **1** is less stable than **3** by 0.6–1.1 kcal $mol^{-1}$, whereas **2** is more stable than **4** by 0.5–1.0 kcal $mol^{-1}$ (Table I).[4]

The ionization potential of the ketone **1** is 0.6 eV (13.8 kcal $mol^{-1}$) higher than for the enol **3**. The enol ion is thus more stable than the keto ion by 14.4–14.9 kcal $mol^{-1}$. This is in line with data for other enol and ketone ions, where the enol ion is more stable by 14–31 kcal $mol^{-1}$.[5] Surprisingly, the IP values are almost identical for the ketone **2** and the enol **4**. This is not easily explained by the structural change and may reflect ionization of **2** at the dimesitylmethyl moiety rather than at the C=O group.

Kinetic-energy release determinations were used to probe for differences between the ketone and enol ions. Enol ions were obtained by direct ionization of **3** and **4** as well as by a four-center

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