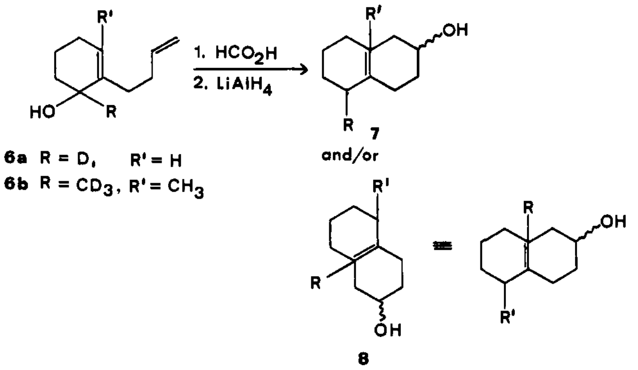

only **8**; (b) concerted ionization–condensation by a "zipper" mechanism (S_N2') would give only **7**;[10] (c) stepwise ionization–condensation via a resonance-stabilized allylic cation (S_N1) should result in a mixture of equal parts of **7** and **8**.

The required alcohols **6a** and **6b** were prepared in a straightforward manner and subjected to formolysis as described in the supplementary material. The resulting product mixtures were reduced with $LiAlH_4$ in ether and the alcohol was isolated by filtration through a silica gel column. The product composition was determined by taking NMR spectra of the purified mixture and comparing them with spectra of products obtained from unlabeled cyclohexenols. They show well-resolved signals for C_3-H, C_1-CH_3 and C_3-CH_3 centered at δ (relative to Me_4Si) 5.35, 1.59, and 1.04 respectively. The cyclization was practically quantitative, and the product alcohols from either **6a** or **6b** showed a 50% reduction in peak intensities for the respective hydrogens in **7a** and **8a** and the respective methyl groups in **7b** and **8b**.[11]

On the basis of these results one can confidently conclude that in intramolecular cationic π-cyclization reactions of Δ^2-cyclohexenol derivatives, the allylic cation is the first formed intermediate (mechanism C). It is sufficiently stable to permit rotation of the side chain and a subsequent indiscriminate attack of the double bond on either one of the equivalent carbon atoms of the allylic system. It is interesting to note that in this respect the less substituted cation derived from **6a** behaves identically with the tertiary allyl cation derived from **6b**.[12]

Reports on kinetic and isotope effect studies of π-cyclization reactions on a series of similar substrates will appear elsewhere.[13]

Supplementary Material Available: Preparation of **6a** and **6b** and their deuterated derivatives (7 pages). Ordering information is given on any current masthead page.

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(10) For an excellent discussion of this "nonstop" mechanism, see: Cornforth, J. W. *Angew. Chem.* **1968**, *80*, 977.

(11) Identical results were obtained in preliminary experiments where the product formation was followed directly in the NMR tube.

(12) One referee raised the question of possible label scrambling *prior* to cyclization which would make the mechanisms a–c undistinguishable. Such internal return is highly improbable on the following grounds: (i) the cyclization in formic acid is almost instantaneous; (ii) solvolysis of unsymmetric substrates (R = H, R' = CH_3) which upon ion-pair return would yield more reactive derivatives shows clean first-order kinetics and normal α-deuterium isotope effects.[13]

(13) The greater part of the, as yet unpublished, material can be found in the Ph.D. Thesis of M. Ladika (University of Zagreb, 1978).

Gas-Phase Oxidation Catalysis by Transition-Metal Cations

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We wish to report the observation, using ion cyclotron resonance (ICR) spectroscopy, of catalytic oxidation cycles involving transition-metal cations and their oxides in the gas phase. For example, oxidation of CO to CO_2 by N_2O is catalyzed by iron cations (Scheme I). This occurs in a two-step process. Fe^+ accepts an oxygen atom from N_2O to give FeO^+ (reaction 1),[1a] and FeO^+ transfers the oxygen atom to CO to produce CO_2, regenerating Fe^+ (reaction 2). The net result is transfer of an oxygen atom from N_2O to CO (reaction 3). This overall process is exothermic by 107 kcal mol^{-1} but does not occur directly at room temperature to any measurable extent.[1b]

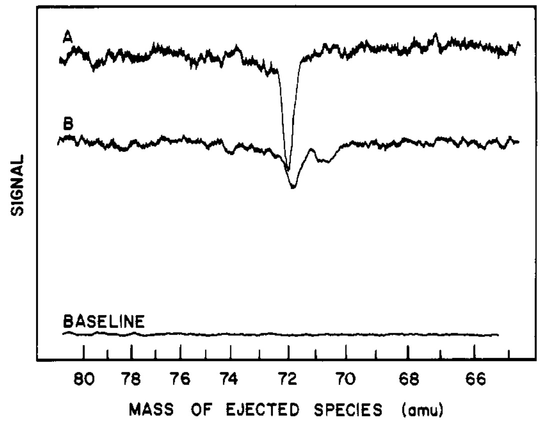
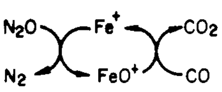


Figure 1. Shown is the ICR signal obtained for Fe^+ while scanning the double-resonance oscillator to eject ions of a given mass from the cell. Trace B is obtained with only N_2O present ($P_{N_2O} = 4.0 \times 10^{-6}$ torr). Trace A results when CO is added to the system ($P_{N_2O + CO} = 4.7 \times 10^{-6}$ torr). The increase in Fe^+ signal after adding CO is due to regeneration of Fe^+ by reaction 2. This is evidenced by the double resonance at *m/e* 72 (FeO^+) which indicates that FeO^+ is reacting to Fe^+.

Scheme I



$$Fe^+ + N_2O \rightarrow FeO^+ + N_2,\ k = 0.7 \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad (1)$$

$$FeO^+ + CO \rightarrow Fe^+ + CO_2,\ k = 9 \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad (2)$$

$$N_2O + CO \rightarrow CO_2 + N_2,\ \Delta H^\circ = -107\ \mathrm{kcal\ mol^{-1}} \quad (3)$$

The experimental arrangement used for this study has been previously described.[2] A pulsed YAG laser is used to produce atomic metal cations inside the ICR cell. Reactions of these ions with neutral gases are investigated by conventional ICR techniques.[3] When Fe^+ is generated in the presence of N_2O, first-order decay of the Fe^+ signal is observed with a corresponding increase of the FeO^+ signal. The observed half-time indicates a rate constant of $k = 0.7 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for reaction 1. Thus at 4×10^{-6} torr of N_2O, 80% of the Fe^+ is converted to FeO^+ after 180 ms. Addition of CO to this system increases the Fe^+ signal and decreases the FeO^+ signal with respect to their previous values with only N_2O present. At 180 ms, for example, the Fe^+ signal is 50% larger than with only N_2O present when 0.7×10^{-6} torr of CO is added. Double-resonance spectra (Figure 1) show that the relative increase in Fe^+ is due to a reaction by FeO^+ that occurs only in the presence of CO. The slight dou-

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(1) (a) Reaction 1 was reported by Allison, J., Ph.D. Thesis, University of Delaware, 1978, p 123. (b) The standard enthalpy change for this reaction was calculated from heats of formation given in: Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(2) (a) Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3794-3798. (b) Uppal, J. S.; Staley, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4144-4149.

(3) For a general description of ICR, see: Lehman, T. A.; Bursey, M. M. "Ion Cyclotron Resonance Spectrometry"; Wiley: New York, 1976.

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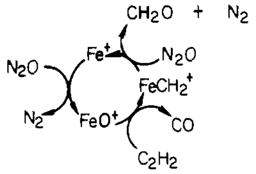
Scheme II



ble-resonance response for FeO^+ to Fe^+ reaction which is observed when only N_2O is present may be attributed to reaction 4. This

$$FeO^+ + N_2O \rightarrow Fe^+ + N_2 + O_2 \qquad (4)$$

minor process is either very slow or due to a small fraction of excited FeO^+ molecules.[4] Delayed-ejection double-resonance experiments show that the Fe^+ produced by reaction 2 reacts again according to reaction 1 and that the complete cycle (Scheme I) occurs repeatedly. No reaction of Fe^+ is observed in the presence of only CO. With N_2O and CO, FeO^+ is the only product observed. By assuming that only reactions 1 and 2 are occurring and using the measured rate for reaction 1, the observed variation of ion abundances with time for Fe^+ and FeO^+ in mixtures of N_2O and CO can be analyzed to give a rate constant of $k = 9 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} for reaction 2. The same value is obtained by analyzing the delayed-ejection results. Reaction 2 is occurring at its expected Langevin rate,[5] i.e., essentially on every collision. Reaction 1 occurs more slowly, on about every sixth collision.

Reactions 1 and 2 involve simple transfer of an oxygen atom from N_2O to Fe^+ and from FeO^+ to CO. The homolytic bond dissociation energy for FeO^+, $D(Fe^+–O)$, therefore must lie between $D(N_2–O)$ = 40 kcal mol^{-1} and $D(CO–O)$ = 127 kcal mol^{-1}.[1b] These limits are consistent with our observations that Fe^+ will also react with O_3 to give FeO^+, $D(O_2–O)$ = 26 kcal mol^{-1}, but that FeO^+ is not produced when Fe^+ is generated in the presence of O_2, $D(O–O)$ = 119 kcal mol^{-1}.[1b]

FeO^+ will transfer oxygen atoms to other acceptors in addition to CO. Thus, evidence for catalytic cycles analogous to Scheme I is also seen in mixtures of N_2O with ethylene, propylene, allene, ethane, and propane. In all of these systems other minor ionic products in addition to Fe^+ are formed when FeO^+ reacts with the organic neutral. These reactions along with other chemistry of transition-metal oxide cations will be reported in a future paper.[6]

With acetylene an interesting three-step catalytic cycle (Scheme II) is observed to occur. FeO^+ reacts in part directly to give Fe^+ (reaction 5), as in Scheme I, but also produces $FeCH_2^+$ eliminating

$$FeO^+ + C_2H_2 \rightarrow Fe^+ + C_2H_2O \qquad (5)$$

$$FeO^+ + C_2H_2 \rightarrow FeCH_2^+ + CO \qquad (6)$$

CO (reaction 6). $FeCH_2^+$ reacts with N_2O to regenerate Fe^+ (reaction 7). The net result of this catalytic cycle (reactions 1,

$$FeCH_2^+ + N_2O \rightarrow Fe^+ + N_2 + CH_2O \qquad (7)$$

6, and 7) is oxidation of acetylene by two N_2O molecules to give CO and formaldehyde (reaction 8). This overall reaction is

$$C_2H_2 + 2N_2O \rightarrow 2N_2 + CO + CH_2O \qquad (8)$$

exothermic by 148 kcal/mol.[1b] The branching ratio for reactions 5 and 6 cannot be determined accurately but appears to be approximately 1:1.

Transition-metal oxide cations can be produced by reaction of N_2O with Ti^+, Zr^+, V^+, Nb^+, and Cr^+ in addition to Fe^+. Catalytic cycles involving M^+ and MO^+ are not observed for these five metals when CO or other simple oxygen acceptors are added. This is because $D(M^+–O)$ is too large in these cases. In fact, for Ti, Zr, and Nb, CO_2 reacts with M^+ to generate MO^+ (reaction 9). In other cases neither the forward nor the reverse of reaction

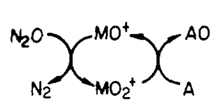
$$M^+ + CO_2 \rightarrow MO^+ + CO \qquad (9)$$

9 is observed, indicating that even in the exothermic direction the reaction is slow. However, further reaction of MO^+ with N_2O occurs in these five systems to give metal dioxide cations (reaction 10). When simple oxygen acceptors, A, are added, evidence for

$$MO^+ + N_2O \rightarrow MO_2^+ + N_2 \qquad (10)$$

a catalytic cycle (Scheme III) involving MO^+ and MO_2^+ is observed in each case. With niobium, N_2O can be replaced by O_2 to give the catalytic cycle. With chromium, CrO_3^+ is also produced but does not appear to participate in a catalytic cycle. Further details of our observations on the ion chemistry of metal cations with oxidants will be reported separately.[7]

Scheme III



The work presented in this communication is the first example of a new type of ion–molecule reaction. Catalysis in gas phase ion–molecule chemistry has been previously reported for the case of slow proton transfer from toluene to the allyl anion mediated by methanol/methoxy anion.[8] The present work is the first report to our knowledge of catalysis in gas-phase positive ion chemistry. Moreover, it is also the first case of catalysis involving transition-metal species. Other reports of gas-phase transition-metal ion chemistry have recently been appearing with increasing frequency.[2,9] Such studies, including the present work, provide thermochemical data and mechanistic insights which are useful in better understanding the behavior of transition-metal ion species. This promises to continue to be a rapidly advancing field.

Acknowledgment. This work was supported by the National Science Foundation by Grant CHE-76-17304.

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[4] Overall, the conversion of two N_2O molecules to an O_2 and two N_2 is exothermic by 39.2 kcal mol^{-1}.[1b]

[5] Calculation of Langevin rates is discussed in Weston, R. E., Jr.; Schwartz, H. A. "Chemical Kinetics"; Prentice-Hall: Englewood Cliffs, NJ, 1972. Polarizability values for CO of $\alpha = 1.95 \times 10^{-24}$ cm^3 and for N_2O of $\alpha = 3.0 \times 10^{-24}$ cm^3 were taken from McQuarrie, D. A. "Statistical Thermodynamics"; Harper and Row: New York, 1973. The calculated rates are $k = 5 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} for reaction 1 and $k = 4 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} for reaction 2.

[6] Kappes, M. M.; Staley, R. H., in preparation.

[7] Kappes, M. M.; Staley, R. H. *J. Phys. Chem.*, submitted for publication.

[8] Brauman, J. I.; Leider, C. A.; White, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 927–928.

[9] For example, see: (a) Cordermann, R. R.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3998–4000. (b) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998–5009. (c) Burnier, R. C.; Carlin, J. J.; Reents, J. J., Jr.; Cody, R. B.; Lengel, R. K.; Freiser, B. S. *J. Am. Chem. Soc.* **1979**, *101*, 7127–7129.

On the Mechanism of the Fischer–Tropsch Reaction. The Chain Propagation Step

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We wish to report results pertaining to the mechanism of the Fischer–Tropsch reaction, i.e., the conversion of CO and H_2 to hydrocarbons, principally a mixture of linear alkanes and alkenes, by passage over heterogeneous transition-metal catalysts.

Since the discovery of the reaction, three separate proposals for the mechanism of the reaction have received dominant consideration; the three differ markedly in the manner in which the C–C bonds of the product are purported to be formed. The first, proposed by Fischer and Tropsch in 1926,[1] suggested that the C–C

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[1] Fischer, F.; Tropsch, H. *Brennst.-Chem.* **1926**, *7*, 97–116; *Chem. Ber.* **1926**, *59*, 830–836.

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