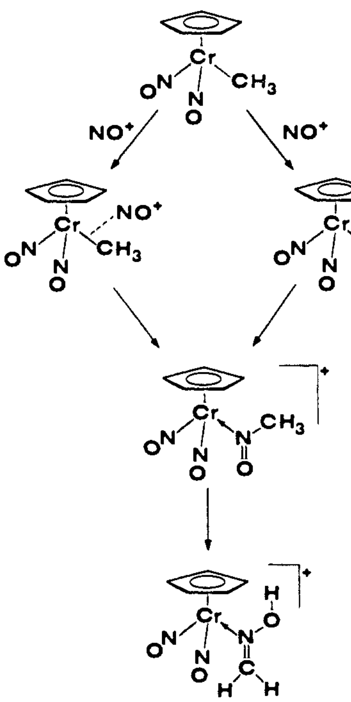
Scheme I



those of free formaldoxime.[10] In valence-bond terms, the bonding within this grouping is thus best represented as

$$Cr \leftarrow N(=CH_2)OH$$

with the ligand functioning as a formal two-electron donor. The hydroxyl H atom of the formaldoxime ligand is also linked by a hydrogen bond [H(10)–F(2) = 2.14 (8) Å] to the counteranion.[11] The spectroscopic properties of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2\{N(CH_2)OH\}]PF_6$[6] can be readily understood in terms of its solid-state molecular structure, thus indicating that the basic structural units persist in solutions.

The two most likely mechanistic pathways for the unprecedented reaction 2 are those involving either oxidatively induced, intramolecular insertion of bound NO into the Cr–CH$_3$ bond[13] or charge-controlled, intermolecular attacks by NO$^+$ at the Cr–CH$_3$ group. At present, we favor the latter pathways (Scheme I)[15] since oxidation of $(\eta^5\text{-}C_5H_5)Cr(NO)_2CH_3$ by $[Fe(phen)_3]^{3+}$ followed by treatment with NO does not afford the formaldoxime product of reaction 2.[18] It thus appears that reaction 2 occurs because $(\eta^5\text{-}C_5H_5)Cr(NO)_2CH_3$ is relatively difficult to oxidize and its Cr–CH$_3$ bond is prone to nonoxidative attack by electrophiles.[19] Experiments designed to determine the scope of this new synthetic route to C–N bonds and to confirm the mechanism of reaction 2 are currently in progress.

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Supplementary Material Available: Tables of fractional coordinates and isotropic and anisotropic thermal parameters for $[(\eta^5\text{-}C_5H_5)Cr(NO)_2\{N(CH_2)OH\}]PF_6$ (4 pages). Ordering information is given on any current masthead page.

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(10) Levine, I. N. *J. Chem. Phys.* **1963**, *38*, 128.

(11) A similar feature has been observed for $[(\eta^5\text{-}C_5H_5)_3Mn_3(\mu_2\text{-}NO)_3(\mu_3\text{-}NOH)]PF_6$.[12]

(12) Legzdins, P.; Nurse, C. R.; Rettig, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 3727.

(13) Related oxidatively promoted alkyl to acyl migratory insertions have been documented.[14]

(14) Magnuson, R. H.; Meirowitz, R.; Zulu, S.; Giering, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 5790 and references therein.

(15) In this scheme, the attack by NO$^+$ is portrayed as being a classical S$_E$2 process.[16] Also, the isomerization of the CH$_3$NO ligand to bound CH$_2$=NOH shown in the last step is probably facilitated by the acidic species present, an inference that has ample literature precedents.[17]

(16) Rogers, W. N.; Page, J. A.; Baird, M. C. *Inorg. Chem.* **1981**, *20*, 3521 and references therein.

(17) Boyer, J. H. In "The Chemistry of the Nitro and Nitroso Groups"; Feuer, H., Ed.; Wiley-Interscience: Toronto, 1969; Part 1.

(18) At room temperature in CH$_2$Cl$_2$, $(\eta^5\text{-}C_5H_5)Cr(NO)_2CH_3$ (ν_{NO} 1777 (s), 1669 (s) cm^{-1}) is completely converted by 1 equiv of $[Fe(phen)_3]^{3+}$ into a $(\eta^5\text{-}C_5H_5)Cr(NO)_2{}^+$-containing product[2] ($\nu_{NO}$ 1846 (s), 1745 (s) cm^{-1}).

(19) Legzdins, P.; Wassink, B., unpublished observations.

Substrate and Positional Selectivity of the Gas-Phase Nitration of Substituted Benzenes by Protonated Methyl Nitrate. The First Example of a Well-Behaved Aromatic Nitration by a Gaseous Cation

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The central role played by electrophilic nitration in the theory of aromatic substitution[1] has stimulated mass spectrometric approaches to its study in the gas phase. Unfortunately, the available results delineate reactivity patterns dominated by processes, e.g., charge exchange and oxygen-atom transfer, peculiar of mass spectrometric conditions and hardly consistent with solution-chemistry data. Thus, NO$_2{}^+$ fails to add to arenes, and the other reagents used, CH$_2$ONO$_2{}^+$ and EtO(NO$_2$)$_2{}^+$, nitrate *deactivated* substrates at *higher* rates.[2-4] Futhermore, the lack of discrimination between isomeric nitrated adducts has prevented so far the crucial evaluation of positional selectivity.

We report a gas-phase ionic nitration whose substrate and positional selectivity, measured with a combination of mass spectrometric and radiolytic techniques, conform to common experience in condensed-phase nitration. The electrophile used, MeO$^+$(H)NO$_2$, belongs to a class of nitrating reagents well-known in solution[6] and is readily obtained in the gas phase, e.g., it represents a major ion in the CH$_4$ chemical ionization (CI) spectrum of methyl nitrate, arising from the exothermic[7] process

$$C_nH_5{}^+ + MeNO_3 \rightarrow C_nH_4 + MeO^+(H)NO_2 \qquad n=1,2 \qquad (1)$$

According to MINDO calculations,[8] the protonated ester in its most stable structure (H_f° = 150.5 kcal mol^{-1}) can be regarded as a nitronium ion "solvated" by methanol, with a binding energy of ca. 34 kcal mol^{-1}. The CI spectra of CH$_4$/MeNO$_3$/C$_6$H$_6$ mixtures display an abundant[9] nitrated adduct, of unknown structure, arising from the process

$$C_6H_6 + MeO^+(H)NO_2 \rightarrow C_6H_6NO_2{}^+ + MeOH \qquad (2)$$

Replacement of C$_6$H$_6$ with C$_6$D$_6$ yields comparable amounts of C$_6$D$_6$NO$_2{}^+$ and C$_6$D$_5$HNO$_2{}^+$. Analogous adducts are formed from

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(1) Cf.: Schofield, K. "Aromatic Nitration"; Cambridge Press: London, 1980.

(2) Benezra, S. A.; Hoffman, M. K.; Bursey, M. M. *J. Am. Chem. Soc.* **1970**, *92*, 7501-7502.

(3) Morrison, J. D.; Stanney, K.; Tedder, J. M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 967-969.

(4) Ausloos, P.; Lias, S. G. *Int. J. Chem. Kinet.* **1978**, *10*, 657-667.

(5) Dunbar, R. C.; Shen, J.; Olah, G. A. *J. Am. Chem. Soc.* **1972**, 6862-6864.

(6) Raudnitz, H. *Chem. Ber.* **1927**, *69*, 738-743. See also ref 1, p 94, and references therein.

(7) Calculations based on the heat of formation of MeO$^+$(H)NO$_2$ given in ref 8 and on data from Cox and Aue [(a) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. (b) Aue, D. H.; Bowers, M. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, p 2-53] lead to ΔH° values of −57 and −22 kcal mol^{-1} for the proton transfer from CH$_5{}^+$ and C$_2$H$_5{}^+$, respectively.

(8) Dewar, M. J. S.; Shanshal, M.; Worley, S. D. *J. Am. Chem. Soc.* **1969**, *91*, 3590-3594.

(9) The CI spectra were recorded at CH$_4$ pressures up to ca. 0.5 torr and a source temperature of 150 °C, using a Hewlett-Packard 5982A quadrupole spectrometer or a ZAB-2F magnetic instrument (Micromass Ltd.). The ionic abundance of the C$_6$H$_6$NO$_2{}^+$ adduct in the CI spectra of CH$_4$/MeNO$_3$/C$_6$H$_6$ mixtures (molar ratios 1:0.016:0.002) ranges from 16% at ca. 0.25 torr to 26% at ca. 0.5 torr.

Table I. Relative Reactivity and Orientation of Substituted Benzenes in the Gas-Phase Nitration by Radiolytically Formed $MeO^+(H)NO_2$ Ions

substrate PhX	rel reactivity[a] $k_{PhX}:k_{PhH}$	orientation[b] % ortho	% meta	% para	partial rate factors[c] f_o	f_m	f_p
toluene	2.9	52	≈4	44	4.5		7.7
fluorobenzene	0.31	26	≈3	71	0.24		1.3
chlorobenzene	0.25	43	11	46	0.32	0.082	0.69
α,α,α-trifluorotoluene	3.7×10^{-3}	d	100	d		0.011	
anisole	3.2	27	*d*	73	2.6		14
mesitylene	5.6		*e*				

[a] Standard deviation ca. 20%, except in the case of trifluorotoluene, ca. 30%. [b] Standard deviation ca. 10%, except for *m*-nitrotoluene and *m*-fluoronitrobenzene, whose reported percentages are crude estimates, owing to their low abundance among isomers. [c] Partial rate factors are omitted when the corresponding products could not be detected, or the yields were so low as to confer a largely approximate character to the data, e.g., in the case of *m*-F and *m*-Me factors. [d] Below detection limit, ca. 2%. [e] Only 2,4,6-trimethylnitrobenzene formed.

PhMe and other aromatics, while double-resonance ICR experiments confirm that $MeO^+(H)NO_2$ is indeed their precursor, consistent with the results of Bursey and co-workers.[2]

The radiolytic experiments involve irradiation of mixtures containing CH_4 (720 torr), $MeNO_3$ (10–15 torr), the aromatic substrate(s) (≤1 torr), and a radical scavenger (O_2, 10 torr), at 37.5 °C in a 220 Gammacell (Nuclear Canada Ltd.) to a dose of 3 Mrad.[10] Analysis of the irradiated samples by GLC and GLC/MS[11] demonstrates significant yields of the expected nitrobenzenes, e.g., G_{+PhNO_2} 1.2 ± 0.2 from PhH. The mass spectrometric data make interpretation of the radiolytic results straightforward. CH_5^+ and $C_2H_5^+$, formed from the radiolysis of CH_4 with a combined $G_{+M} = 2.8$,[12] promote nitration according to eq 1 and 2. Deprotonation of the nitrated adducts, which obviously contain a C–N bond, by any gaseous base, including the substrate itself, eventually yields neutral nitrobenzenes. The ionic character of the nitration is independently demonstrated by the dramatic depression of the yields caused by additives (e.g., NH_3) which intercept $C_nH_5^+$[13] and $MeO^+(H)NO_2$. The role of the latter as the nitrating agent emerges from the observation that replacing CH_4 with $i\text{-}C_4H_{10}$ nearly suppresses the formation of $PhNO_2$ ($G_{+M} \leq 0.015$), owing to the inability of $t\text{-}C_4H_9^+$ to protonate $MeNO_3$.[14]

The radiolytic results are summarized in Table I. With the exception of those concerning anisole, the partial rate factors fit a reasonably linear (correlation coefficient 0.983) Hammett's plot,[15] whose ρ^+ value, −3.3, characterizes the gas-phase nitration as a typically electrophilic substitution. As a comparison, typical ρ^+ values of aromatic nitration are ca. −9 (HNO_3 in H_2SO_4) and −6 ($AcONO_2$ in Ac_2O).[16] The lower than expected reactivity of anisole is explained by the incursion of the proton transfer

$$PhOMe + MeO^+(H)NO_2 \rightarrow PhO^+(H)Me + MeNO_3 \qquad (3)$$

Indeed, anisole is the only substrate investigated containing a n-type site more basic than $MeNO_3$.[17] Since exothermic proton transfer processes involving n-type bases generally proceed at nearly unit collision efficiency in the gas phase,[18], competition by reaction 3 provides a neat explanation of the abnormally low nitration rate of anisole.

In conclusion, the present preliminary results show that the combination of mass spectrometry with radiolytic techniques and use of a suitable electrophile allow the study of aromatic nitration in the gas phase without incurring into earlier, disturbing inconsistencies with solution-chemistry trends.

Much scope exists for exploiting the approach outlined in this report, since the unique properties of the gaseous reaction environment allow direct comparison with theoretical results and construction of crucial, quantitative arguments bearing on fundamental aspects of aromatic reactivity, long debated in solution chemistry.[19]

Warning: Methyl nitrate may explode if overheated in closed vessels. Attempts to shatter fragile Pyrex ampules containing liquid $MeNO_3$ may result in explosions.

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(10) For details, cf.: Cacace, F. *Radiat. Phys. Chem.* **1982**, *20*, 99–110 and references therein.

(11) The following columns were used: (i) A 3.3-m-long, 3-mm-i.d. glass column, packed with SP-2100 (20% w/w) and Carbowax 1500 (1%) on 100–120 mesh Supelcoport, operated at 110–130 °C. (ii) A 25-m-long, 0.25-mm-i.d. silica column, coated with methylsilicone fluid, operated from 80 to 120 °C. (iii) A 25-m-long, 0.53-mm-i.d. silica column, coated with OV-101, operated from 60 to 120 °C.

(12) Ausloos, P.; Lias, S. G.; Gorden, R., Jr. *J. Chem. Phys.* **1963**, *39*, 3341–3348. From this value, the $PhNO_2$ yield can be estimated to be ca. 40%.

(13) (a) Meot-Ner, M. *J. Am. Chem. Soc.* **1979**, *101*, 2589–2595. (b) Attinà, M.; Cacace, F.; Giacomello, P.; Speranza, M. *J. Am. Chem. Soc.* **1980**, *102*, 6896–6898.

(14) From the data of ref 8, the PA of $MeNO_3$ can be calculated to be ca. 185 kcal mol^{-1}, vs. 197 kcal mol^{-1} of isobutene, ref 7b.

(15) While it is questionable whether ρ^+ values from solution-chemistry reactions can be extended with any degree of accuracy to the gas phase, previous attempts have revealed no conspicuous discrepancies, cf.: Lau, Y. Y.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 7452–7453.

(16) Coombes, R. G.; Crout, D. H. G.; Hoggett, J. G.; Moodie, R. R.; Schofield, K. *J. Chem. Soc. B* **1970**, 347 and references therein.

(17) From the calculated PA of the oxygen atom of PhOH (cf.: De Frees, D. J.; Mc Iver, R. T., Jr.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 3853–3854 and the basicity increase due to Me substitution, the oxygen atom of PhOMe can be expected to be assuredly more basic than $MeNO_3$.

(18) Su, T.; Bowers, M. T., ref 7b, Vol. 1, pp 83–118.

(19) For a discussion concerning aromatic nitration at encounter rate, and the question of π-type vs σ-type transition states, see ref 1 and: (a) Olah, G. A. *Acc. Chem. Res.* **1971**, *4*, 240–248. (b) Ridd, J. H. *Acc. Chem. Res.* **1971**, *48* 248–253.

Footballene: A Theoretical Prediction for the Stable, Truncated Icosahedral Molecule C_{60}

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This paper presents preliminary theoretical evidence for the stable molecule C_{60}. In the proposed molecule, each carbon atom is sp^2 hybridized and bonded to three other carbon atoms. Hence C_{60} is an "alkene" containing no hydrogen and approximates a spherical shell of graphite.

Any structure with 12 pentagonal rings and 20 hexagonal rings satisfies the requirements of chemical bonding and constitutes a roughly spherical molecule, as shown below. The pentagonal rings may be viewed as "defects" compared to the unstrained hexagonal rings. The most symmetrical possible structure is the truncated icosahedron (Figure 1a). The pentagonal rings sit as far as possible from each other, at the vertices of an icosahedron (Figure 1b). For convenience this molecule is called here "footballene" ("soccerballene" in the US). Each carbon atom is equivalent to every other carbon atom, being the vertex joining a pentagon and

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