Incorporation of Neutral Molecules into Alkali Halides ("Salting"). Room-Temperature Composites from Normally Immiscible Components and Room-Temperature Matrix Isolation

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We have prepared stable materials containing 0.1–1% of a volatile nonionic guest "salted" in an alkali halide matrix. The term "salting" acknowledges the ancient practice of preserving perishables by mixing with salt.[2,3]

Codeposition of vapors on a cold surface can yield intimate mixtures, even of components immiscible under equilibrium conditions.[4–7] We wish to identify inert and/or reactive host materials stable as room-temperature solids, suitable for deposition as vapor, and capable of permanently incorporating guest molecules for high-temperature matrix isolation. While organic matrices with good equilibrium solubility for organic guests are common,[8–10] the only previously reported vapor-deposited organic–inorganic composites of interest here involve metals as hosts.[11,12]

Alkali halides, high-melting solids suitable for optical and magnetic resonance spectroscopy, have been used as single-crystal host materials doped with impurity ("color") centers[13] by cocrystallization with ionic guests. Doping by equilibration with a vapor requires temperatures close to the melting point of the host, prohibitive for organic substrates.[14]

We find that cocondensation of organic vapors with excess alkali halide vapor on a 77 K surface and warming to 25 °C in vacuo produce host microcrystals[15] incorporating the volatile guest. Permanency of incorporation was tested by heating to 100 °C under 10^{-3} to 10^{-4} torr for 1 h. Such treatment removes all volatile material that is adsorbed on the surface of the host (and all volatile components from samples produced by mere mechanical mixing of the components and pressing[16]). The presence of the guest was detected by IR and UV absorption, fluorescence, and MAS NMR spectra of the solids. It can be recovered upon dissolution in water.[17] Benzene, naphthalene, anthracene, diphenylmethane, toluene, *p*-dichlorobenzene, 2,6-dichlorophenol, dodecamethylcyclohexasilane, 1-adamantanol, 1-(2-hydroxyethyl)adamantane, 1-azidoadamantane, and iron pentacarbonyl incorporated both in NaCl and in CsI, while chlorobenzene, phenol, *p*-fluorophenol, anisole, and acetophenone incorporated in CsI but not NaCl. Pyrrole incorporated in neither. KBr behaves like CsI, and a series of saturated C_5 and C_6 hydrocarbons incorporated readily. In general, nonpolar materials incorporate best.

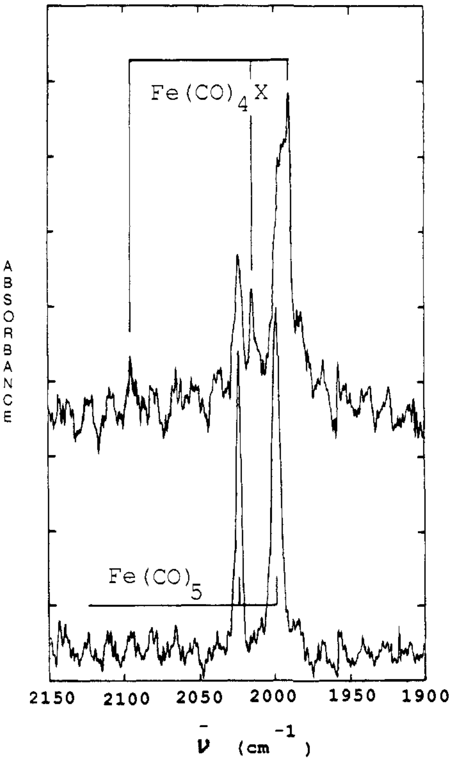

Figure 1. FT-IR spectrum of iron pentacarbonyl in isopentane/potassium bromide matrix at 20 K. Bottom curve, before irradiation; top curve, after irradiation at 308 nm.

The permanency of the incorporation is astonishing. For instance, naphthalene remains in CsI after 2 h at 450 °C or grinding followed by ultrasound (10 h, 25 °C). Several samples remained unchanged for 2 years.

Considering the extreme guest–host incompatibility, it is not surprising that the salted guest molecules are aggregated (cf. micelles), judging by the IR spectra of phenol and alcohols and UV absorption and emission of naphthalene and anthracene. Moreover, the spectra show that UV irradiation (254 nm) of pellets pressed ($<2 \times 10^4$ psi) from our materials produces the photodimer from salted anthracene, tetramesityldisilene[18] from 2,2-dimesitylhexamethyltrisilane salted in KBr, azahomoadamantene dimer[19] from 1-azidoadamantane in KBr, and $Fe_2(CO)_9$ + CO[20,21] from $Fe(CO)_5$ in KBr or CsI. Thermal reversal of the last-named

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[1] On leave of absence from the Institute of Applied Radiation Chemistry, Technical University of Lodz, Poland.

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[15] Their X-ray diffraction powder pattern is indistinguishable from that of an undoped alkali halide, but under a scanning electron microscope an undoped and a doped sample of a vacuum-deposited alkali halide generally appear quite different. Typical grain size is 0.5–5 μm. The actual deposition temperatures are clearly higher than 77 K in view of the large vaporization heats of alkali halides: NaCl, 40.81; KBr, 37.06; CsI, 35.93 kcal/mol. *Langes Handbook of Chemistry*, 11th ed.; Dean, J. A., Ed.; McGraw-Hill: New York, 1973; pp 9-72–9-84.

[16] See, e.g.: Hartman, K. O.; Hisatsune, I. C. *J. Phys. Chem.* **1965**, *69*, 583.

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[20] The same reaction occurs upon irradiation of an argon matrix containing poorly isolated $Fe(CO)_5$ (>1:1000 matrix ratio).[21]

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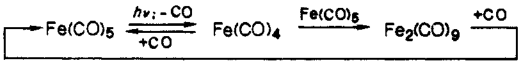
process is quantitative [first-order $k = (2.8 \pm 0.1) \times 10^{-6}\ s^{-1}$ at 27 °C; this ordinarily requires high CO pressures[22]], demonstrating that even the small CO molecules are trapped next to $Fe_2(CO)_9$ within microcavities in the host. Scanning electron microscope (150000×) reveals $Fe(CO)_5$ and $W(CO)_6$ salted in KBr as dimensionless dots imaging as the respective metal; these guest aggregates are at most 10 Å in diameter.

Single-molecule isolation is an important goal. We have succeeded in isolating salted $Fe(CO)_5$ using a three-component system. Codeposition of $Fe(CO)_5$, an alkane (*n*-pentane, isopentane, neopentane, cyclopentane, or 3-methylpentane), and KBr (1:10:2000) yielded a material with sharp IR bands of $Fe(CO)_5$ (Figure 1). After a time amply sufficient to convert $Fe(CO)_5$ salted in KBr to $Fe_2(CO)_9$ + CO, room-temperature UV irradiation of $Fe(CO)_5$ cosalted with an alkane in KBr had no effect. Extended irradiation eventually destroyed all carbonyl IR bands, but even then, no $Fe_2(CO)_9$ was detected.

We propose that the ternary material contains $Fe(CO)_5$ molecules mutually isolated within alkane-filled microcavities in the host. Indeed, while irradiation (308 nm) at 20 K rapidly converts the binary composite to $Fe_2(CO)_9$ and then slowly to $Fe_2(CO)_8$,[23] it converts the ternary material to CO and the C_{3v} form of $Fe(CO)_4$ (Figure 1). This is the stable form of $Fe(CO)_4$ when stabilized by a weak ligand in the fifth coordinating position,[21] perhaps best viewed as $Fe(CO_4)X$ (X = alkane or Br^-). Upon warmup, $Fe(CO)_5$ is reformed quantitatively. Thus, the photochemistry of salted $Fe(CO)_5$ can be summarized as follows:



$$Fe(CO)_5 \underset{+CO}{\overset{h\nu;\,-CO}{\rightleftharpoons}} Fe(CO)_4 \xrightarrow{Fe(CO)_5} Fe_2(CO)_9 \xrightarrow{+CO} Fe(CO)_5$$

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A Comment on the Recently Proposed Mechanism for the Oxidation of Olefins with $PdCl(NO_2)(CH_3CN)_2$

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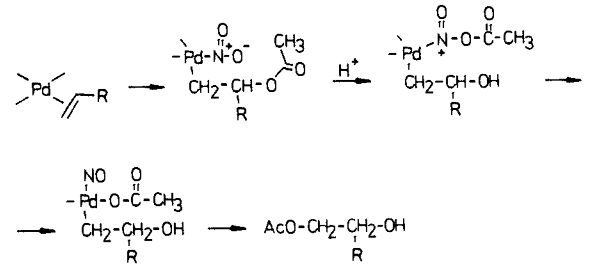
Oxidation of olefins using nitro complexes of palladium(II) has recently attracted attention.[2-4] Depending on the reaction conditions, $Pd(Cl)(NO_2)(CH_3CN)_2$ has been reported to selectively catalyze the oxygen oxidation of olefins to either epoxides, ketones, or glycol monoacetates.[2-4] Mares and co-workers[4] recently reported that oxidation of terminal olefins by $Pd(Cl)(NO_2)(CH_3CN)_2$ (catalytic or stoichiometric) in acetic acid afforded approximately equal amounts of 2-acetoxy-1-alkanol and 1-acetoxy-2-alkanol as the main products. Furthermore, when the nitro group was labeled with ^{18}O, the ^{18}O label was exclusively in the acetate group of the products. To account for these results they suggested a mechanism via an acetoxypalladation, followed by an acetyl migration to an oxygen in the coordinated NO_2 group and subsequent acetoxy migration to palladium and reductive elimination (Scheme I).

Scheme I. Mares's Mechanism[4]

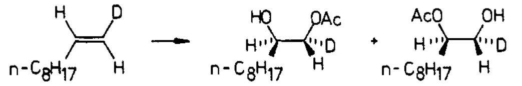


There are two features with the mechanism proposed by Mares that to us seemed inconsistent with known palladium chemistry. First, the mechanism would require an approximate 1:1 ratio of Markovnikov and anti-Markovnikov acetoxypalladation. Under the conditions used, however, one would expect a high regioselectivity for acetate attack at the nonterminal carbon in the π-olefin complex, in accordance with known acetoxypalladation and oxypalladation reactions.[5,6]

Second, the mechanism would require a reductive elimination between an alkyl group and an oxygen nucleophile. There are hitherto no known examples of such reductive eliminations in palladium chemistry, and a recent ab initio ECP calculation suggests that such a process is highly unlikely due to the low orbital energy of the palladium–oxygen bond.[7] We therefore decided to study the mechanism of this glycol monoacetate process.

Acetoxypalladation of olefins is known[8] to occur with trans stereochemistry across the double bond. Since the mechanism suggested by Mares[4] requires the palladium–carbon bond to be cleaved with retention of configuration at carbon, the result would be an overall trans addition of OH and AcO across the double bond. A simple way of testing Mares's mechanism would therefore be to study the stereochemistry of the glycol monoacetate formation from the olefin.

Reaction of a 2-fold excess of (*E*)-1-deuterio-1-decene[9] with $Pd(Cl)(NO_2)(CH_3CN)_2$[10] in acetic acid under air atmosphere for 2 h[11] afforded **1** and **2** in approximately equal amounts according to GLC, HPLC, and ^1H NMR. Small amounts of 2-decanone were also formed, the ratio 2-decanone to glycol monoacetate being 1:4 according to GLC. Separation of the glycol monoacetates **1** and **2** by preparative HPLC (silica, hexane/ethyl acetate =



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(2) (a) Andrews, M. A.; Kelly, K. P. *J. Am. Chem. Soc.* **1981**, *103*, 2894. (b) Andrews, M. A.; Cheng, C. W. F. *Ibid.* **1982**, *104*, 4268. (c) Andrews, M. A.; Chang, T. C. T.; Cheng, C. W. F. *Organometallics* **1985**, *4*, 268.

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(11) The conversion of 1-decene-d_1 was complete after this reaction time and the isolated yield of 1-decene-d_1 glycol monoacetates was approximately 60% based on the olefin.

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