(8) Brown, H. C.; Kirshnamurthy, S. *J. Am. Chem. Soc.* **1972**, *94*, 7159.

(9) Had hydroxymethylation of **8** occurred from the top face (axially) and hydride reduction occurred normally to give the axial hydroxyl at C(3), acetonide formation would be impossible without converting ring A to a boat conformer.

(10) It is essential that the pyrolysis apparatus be carefully neutralized and silylated (bis(trimethylsilyl)acetamide) prior to use.

(11) Arnold, R. T.; Hoffman, C. *Synth. Commun.* **1972**, *2*, 27.

(12) Johnson, W. S.; Werthemann, Bartlett, W. R.; Brocksom, J.; Lee, T.; Faulkner, D. J.; Petersen, M. *J. Am. Chem. Soc.* **1970**, *92*, 741.

(13) Ireland, R. E.; Mueller, R. *J. Am. Chem. Soc.* **1972**, *94*, 5898.

(14) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342.

(15) Merour, J. Y.; Roustan, J. L.; Charrier, C.; Collin, J.; Benaim, J. *J. Organomet. Chem.* **1973**, *51*, C24.

(16) The total synthesis of aphidicolin has also been accomplished by Professor Trost and his colleagues, and we congratulate him on his achievement. See Trost, B. M.; Nishimura, Y.; Yamamoto, K. *J. Am. Chem. Soc.*, preceding paper in this issue.

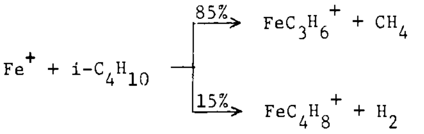
John E. McMurry,* Alex Andrus, Gary M. Ksander
John H. Musser, Mark A. Johnson
Thimann Laboratory, University of California
Santa Cruz, California 95064

Received November 8, 1978

Cleavage of Alkanes by Transition Metal Ions in the Gas Phase

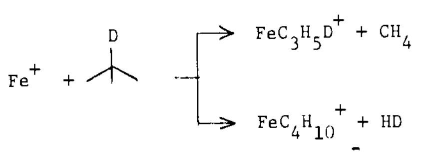
Sir:

Oxidative addition of covalent bonds to metals is common in the chemistry of transition metals in lower oxidation states. There is little evidence in the literature, other than a recent report by Davis and Klabunde,[1] that suggests that carbon–carbon bonds of alkanes add oxidatively to transition metals. We report here observation of gas-phase ion–molecule reactions in which transition metal ions cleave alkanes. Reaction 1, for example, is observed between Fe^+ generated by electron impact on $Fe(CO)_5$ and i-C_4H_{10}. The extent of conversion to products observed in our ion cyclotron resonance spectrometer can only be accounted for by a rapid ($k \geq 10^{-10}$ cm^3 molecule^{-1} s^{-1}) bimolecular process.[2] Double resonance unambiguously identifies the Fe^+ as the source of the product ions. The branching ratio and stoichiometry of the products is confirmed by the reactions of i-C_4D_{10}.



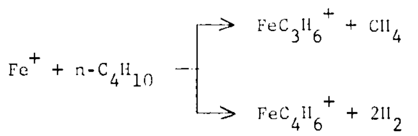
$$Fe^+ + i\text{-}C_4H_{10} \longrightarrow \begin{cases} \xrightarrow{85\%} FeC_3H_6^+ + CH_4 \\ \xrightarrow{15\%} FeC_4H_8^+ + H_2 \end{cases} \quad (1)$$

Several mechanisms might be postulated to account for the observed products. The reaction of 2-deuterio-2-methylpropane, however, eliminates some possibilities (see eq 2). The indicated isotopic variants of the products are the only ones observed indicating they account for at least 90% of the products in each case.



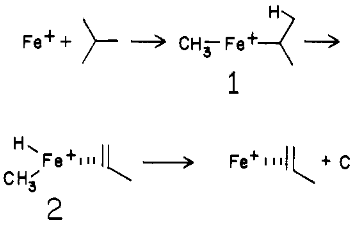
(2)

In addition to reacting with isobutane, Fe^+ undergoes reaction 3 with n-butane. Determination of the branching ratio is complicated in this instance by the presence of several ions in the mass spectrum of $Fe(CO)_5$ with the same masses as possible product ions. The first channel is four or five times as fast as the second. The possibility of $FeC_2H_4^+$ and $FeC_4H_8^+$ products cannot be completely eliminated. Co^+ and Ni^+, formed by electron impact on $Co(NO)(CO)_3$ and $Ni(CO)_4$, react with n-C_4H_{10} to form products analogous to those of eq 3. Ti^+ formed by electron impact on $TiCl_4$ reacts with n-C_4H_{10} to form only $TiC_4H_8^+$ and $TiC_4H_6^+$ products.

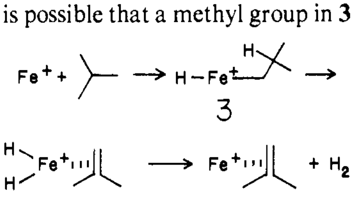


$$Fe^+ + n\text{-}C_4H_{10} \longrightarrow \begin{cases} \longrightarrow FeC_3H_6^+ + CH_4 \\ \longrightarrow FeC_4H_6^+ + 2H_2 \end{cases} \quad (3)$$

A mechanism for the cleavage reaction consistent with our observations is outlined in reaction 4. This mechanism is analogous to that for dehydrohalogenation of alkyl and aromatic halides by Fe^+ [3-5] and accounts for the elimination of methane and the retention of the label in reaction 2. It does not account for the H_2 loss channel. A mechanism such as reaction 5 beginning with attack on the C–H bond is required to account for H_2 loss. It is possible that a methyl group in **3** could migrate to the metal forming **2** which could then lose methane. Hence both reaction channels could pass through **3** and **1** could be unimportant. In either case, at some point in the mechanism carbon–carbon bond cleavage must be dominant over carbon–hydrogen bond cleavage to give the observed product distribution.



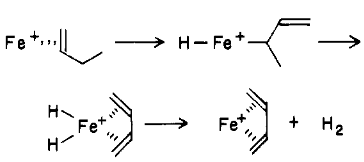
(4)



(5)

We have previously reported the reaction of Fe^+ with CH_3I to form $FeCH_3^+$ from which we deduce that $D(Fe^+–CH_3) >$ 56 kcal/mol.[3] This result combined with $D(CH_3–i\text{-}C_3H_7) =$ 84 kcal/mol[6] indicates that formation of **1** is exothermic if $D(CH_3Fe^+–i\text{-}C_3H_7) >$ 28 kcal/mol, well within the range of measured metal-alkyl radical bond strengths.[3] If we assume that $D(Fe^+–CH_3) \simeq D(Fe^+–i\text{-}C_4H_9)$, then (noting that $D(H–i\text{-}C_4H_9) =$ 98 kcal/mol[6]) formation of **3** will be exothermic if $D(i\text{-}C_4H_9Fe^+–H) >$ 42 kcal/mol. This is certainly a reasonable possibility since it has been reported that $D(Fe(CO)_5^+–H) =$ 74 kcal/mol.[7] Hence formation of either **1** or **3** seems thermodynamically feasible.

We note that either proposed mechanism (initial C–C insertion or initial C–H insertion) can account for the cleavage of n-C_4H_{10} by the metal ions. The $FeC_4H_6^+$ product is readily accounted for by initial formation of $FeC_4H_8^+$ in a process analogous to reaction 5 followed by a second metal insertion into an allylic carbon–hydrogen bond as indicated in reaction 6.



(6)

Acknowledgments are made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work and to the NSF for partial support of this work under Grant No. CHE77-09952.

References and Notes

(1) Stephen C. Davis and Kenneth J. Klabunde, *J. Am. Chem. Soc.*, **100**, 5973 (1978).

0002-7863/79/1501-1332$01.00/0

(2) For a review of ion cyclotron resonance techniques, see J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22,** 527 (1971).
(3) J. Allison and D. P. Ridge, *J. Organomet. Chem.*, **99,** C11 (1975).
(4) J. Allison and D. P. Ridge, *J. Am. Chem. Soc.*, **98,** 7445 (1976).
(5) T. G. Dietz, D. S. Chattelier, and D. P. Ridge, *J. Am. Chem. Soc.*, **100,** 4905 (1978).
(6) Based on heats of formation in H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data*, **6,** Suppl. 1 (1977).
(7) Based on the proton affinity of $Fe(CO)_5 = 204 \pm 3$ kcal/mol (M. S. Foster and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97,** 4808 (1975)) and the ionization potential of $Fe(CO)_5 = 7.95$ eV.

J. Allison, R. B. Freas, D. P. Ridge*
Department of Chemistry, University of Delaware
Newark, Delaware 19711

Received October 26, 1978

Multicarrier Transport: Coupled Transport of Electrons and Metal Cations Mediated by an Electron Carrier and a Selective Cation Carrier[1]

Sir:

Coupled flow of different substrates across membranes plays a fundamental role in biology[2] and may have important practical applications. The realization of artificial systems displaying such properties should allow one to isolate a given component of a complex natural process and thus provide models for detailed mechanistic studies as well as for the evaluation of practical uses.

We report here an artificial system which performs selective transport of alkali cations coupled to the simultaneous flow of electrons in the same direction (symport) across a membrane containing an electron carrier and a cation carrier.[2b]

Several artificial electron transport systems have been reported.[1-5] Electron transfer in phospholipid vesicles occurs when quinone or dibutylferrocene is present and is affected by ionophores or uncouplers such as valinomycin or nigericin.[2] We have previously reported electron transport across supported liquid membranes using menadione and dibutylferrocene as electron carriers, and we have used this system to demonstrate light-driven electron transport by photochemical generation of a reducing agent.[1] It should be possible to couple such electron flow to the symport or antiport of another species, just as amino acid transport may be pumped by a pH gradient or an ion gradient.[6] This has been shown to occur in the counterflow of electrons and picrate anions.[5,7] The use of a carrier for the coupled species would allow control of the selectivity of the transport.

In the artificial systems mentioned above, the nature of the electron carrier determines the species which is coupled to electron transport in order to maintain charge neutrality in the membrane phase. Quinone type carriers couple to proton transport ($2e^- + 2H^+$) since the reduced form is hydroquinone. Ferrocene is typical of carriers which are neutral when reduced and positive when oxidized and thus can be coupled to anion transport.[7] In order to demonstrate coupled cation transport, it is necessary to choose a carrier which is negative when reduced and neutral when oxidized.

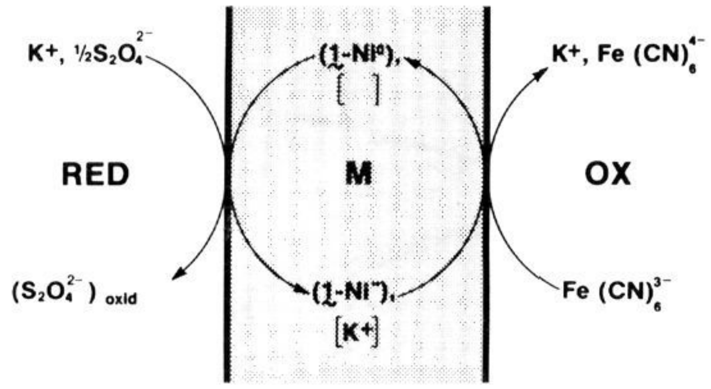
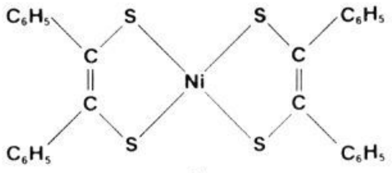
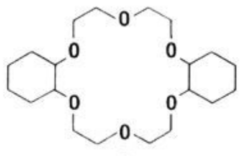


Figure 1. Representation of the mechanism of redox driven potassium cation transport using an electron and a cation carrier. (**1**-Ni^0) and (**1**-N_i^-) are the oxidized and reduced form of the electron carrier, the nickel bisdithiolene complex **1**; [ ] and [K^+] are the macrocyclic ligand, **2**, and its K^+ complex.



1

The present system performs *electron/cation symport* mediated by a nickel bisdithiolene electron carrier, **1,** and a selective carrier for alkali cations, dicyclohexyl-18-crown-6, **2,** dissolved in a diphenyl ether membrane, M, separating two



2

aqueous phases. The nickel bisdithiolene complex may undergo redox reactions at the interfaces with suitable redox reagents, (**1**-Ni^0)/(**1**-Ni^-) = 0.134 V vs. Ag/AgCl.[8] A number of macrocyclic ligands of different types have been shown to transport alkali metal cations[9-11] by solubilizing inorganic salts in apolar media via formation of macrocyclic cation inclusion complexes;[12] macrocycle **2** is a selective carrier for potassium ions.[10] One of the aqueous phases, RED, contains a reducing agent, sodium dithionite ($E_0 = -1.13$ V[13]) and the other, OX, an oxidizing species, potassium ferricyanide ($E_0 = 0.36$ V[13]) (Figure 1[14]).

The processes occurring in the present system are represented in Figure 1. Figure 2 and Table I display results ob-

Table I. Experimental Parameters and Rates of K^+ and e^- Transport[a]

	aqueous phases, initial concn (10^{-3} M)						rate (μmol/h·μmol of **1**)[b]		
	RED		OX		M phase, μmol		RED,	OX	
expt	$Na_2S_2O_4$	K^+	$Na_3Fe(CN)_6$	K^+	**1**	**2**	K^+	K^+	e^-
1	50	160	1.1	0	0.24	3.1		9.3	7.9
2	9.9	0.53	1.0	0.67	0.31	3.6	3.7	4.7	4.3
3	9.8	2.1	1.1	2.5	0.35	3.6	5.8	4.0	5.4
4	50	160	1.1	0	0	3.5		0	0
5	9.7	0.5	1.0	0.64	0	3.4	0	0	0
6	50	160	1.1	0	0.27	0		0	0
7	9.8	1.2	1.1	1.4	0.32	0	0	0	<0.46
8	50	0	1.1	0	0.31	3.9			1.3
9	9.9	0	1.1	0	0.29	3.5			1.3

[a] Buffer conditions: RED phase, expt 1, 4, and 6, 0.1 M K_2HPO_4/KH_2PO_4, expt 8, 0.1 M Li_2HPO_4/LiH_2PO_4, expt 2, 3, 5, 7, and 9, 0.05 M Li_2HPO_4/LiH_2PO_4; OX Phase, same as corresponding RED phase except expt 1, 4, and 6 were 0.1 M Li_2HPO_4/LiH_2PO_4. [b] K^+ and e^- transport rates are the rates of change of K^+ and K^+ and $Fe(CN)_6{}^{3-}$ concentrations in RED and OX phases, respectively; rates are normalized to the quantity of **1** in the membrane.

0002-7863/79/1501-1333$01.00/0