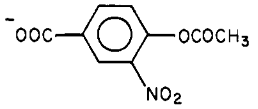
The kinetic runs were *biphasic*, each consisting of two sequential pseudo-first-order reactions, a "fast" process (k_ψ^{f}) accounting for 90–96% of PNPA cleavage and a "slow" reaction (k_ψ^{s}) accounting for the remainder. A typical result appears in Figure 2. Rate constants ($r > 0.999$) for both reactions were readily determined by standard methods and are recorded as a function of [**1**] in Table I. For reasons discussed below, we identify k_ψ^{f} with reactions occurring on the outer surface of vesicular **1** and k_ψ^{s} with reactions occurring *within* vesicular **1**. Both k_ψ^{f} and k_ψ^{s} are relatively independent of experimental kinetic method (A or B), but *only* k_ψ^{f} meaningfully responds to variation of [**1**] and does so in a manner reminiscent of the behavior of heptanethiol + $R_2N^+Me_2$ vesicles.[13]

Vesicular [**1**] shows $k_\psi^{f,\max} = 4.9\ s^{-1}$ at [**1**] = 3.6×10^{-3} M. Plotting $1/k_\psi^{f}$ vs. 1/[**1**] (using data for which [**1**] ≤ 3.6×10^{-3} M) in the Lineweaver Burk analysis commonly employed for micellar reactions[6] gives $k_v = 9.8 \pm 0.3\ s^{-1}$ and $K/N = 276 \pm 2\ M^{-1}$, where k_v represents the rate constant for cleavage of externally bound PNPA. Assuming an aggregation number $N \sim 14\,000$,[24] the binding of PNPA to vesicular **1** is characterized by $K \sim 3.9 \times 10^6\ M^{-1}$. In PNPA cleavage, vesicular **1** is superficially comparable to micellar **2**, for which $k_\psi^{\max} = 2.16\ s^{-1}$ (pH 7) or $9.71\ s^{-1}$ (pH 8), but **2** requires higher concentrations (~0.02 M) to reach optimal efficiency. Assuming $N \sim 70$[14a] for micellar **2**, $K \sim 2400\ M^{-1}$ for binding PNPA,[14a] about 1600 times less than K for vesicular **1**. Defining k_{cat} as $k_\psi^{\max}$/[surfactant], k_{cat} = 1360 L/mol·s for vesicular **1** and ~300 L/mol·s for micellar **2** under roughly comparable conditions. Vesicular **1** and heptanethiol/$R_2N^+Me_2$ (R = 85% n-C_{18}, 15% n-C_{16}) vesicles[13] are kinetically comparable in terms of k_{cat} for PNPA cleavage.[25]

Most intriguing is the observation of "outside" and "inside" thiolytic PNPA cleavages by vesicular **1**. This kinetic dichotomy persists with *p*-nitrophenyl hexanoate, and we believe that both substrates migrate across the outer bilayer of vesicular **1** at rates at least comparable to that of cleavage.[26] Due to the multilamellar nature of vesicular **1**, there are more binding sites on the interior lamellae than on the exterior surface. It is thus possible that the overall rate of substrate diffusion into the vesicles exceeds the overall rate of substrate exit so that biphasic kinetics attend substrate thiolysis whether the **1**/substrate systems are constructed by coinjection or subsequent injection methods.

Ionic substrates, however, cannot as easily cross vesicular membranes;[3c] anionic substrates in particular should be bound to one or the other side of a cationic bilayer. Accordingly, the anionic PNPA analogue, 4-acetoxy-3-nitrobenzoate, **8**,[27] was cleaved by 1.03×10^{-3} M vesicular **1** at pH 8.1. Vesicular **1** prepared by coinjection, where **8** can bind to both interior and exterior surfaces of the vesicles, displayed biphasic kinetics for cleavage of **8** (method A), with k_ψ^{f} (96% of reaction) = $2.5\ s^{-1}$ and $k_\psi^{s} = 0.099\ s^{-1}$. Vesicular **1**, prepared by method B and *subsequently* reacted with **8**, displayed only monophasic kinetics (≥99% of reaction) with $k_\psi^{f} = 2.4\ s^{-1}$.[28] Note that k_ψ^{f} is identical under both conditions and comparable to the analogous k_ψ^{f} value for PNPA (Table I).



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These results offer strong support for associating the biphasic esterolytic reactions with internal and external vesicular thiol groups. These may differ in reactivity for a variety of reasons. We second Fendler's observation that "functionalized surfactant vesicles hold the key to new types of highly relevant and. . .fascinating chemistry".[2a] We are vigorously exploring the chemistry of **1** and related functional vesicles.

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[24] This value can be estimated for dihexadecyldimethylammonium bromide vesicles from data in ref 8.

[25] On the basis of [heptanethiol], we estimate $k_{cat} \sim 1460$ L/mol·s from the data in ref 13.

[26] Other large hydrophobic molecules cross vesicular bilayers at comparable rates; cf. M. Almgren, *J. Am. Chem. Soc.*, **102**, 7882 (1980).

[27] C. G. Overberger, T. St. Pierre, N. Vorchheimer, J. Lee, and S. Yaroslavsky, *J. Am. Chem. Soc.*, **87**, 296 (1965).

[28] Preliminary results indicate that cyanation of vesicular **1** by 2-nitro-5-(thiocyanato)benzoate[29] anion using subsequent injection (method B) also occurs with monophasic kinetics.

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Iron and Ruthenium Carbonyl Catalyzed Reductive Carbonylation of Nitro Compounds by Sodium Methoxide. A Significant Effect of the Metal on the Reaction Course

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Metal carbonyl induced reduction and reductive carbonylation reactions are important processes of considerable industrial interest. The nitro functionality has played a major role in this chemistry. One of us has recently demonstrated that nitro compounds could be reduced to amines by the clusters triiron[2] or triruthenium[3] dodecacarbonyl under gentle conditions using phase–transfer catalysis. Although the same products were obtained by using either of the metal carbonyls, there were significant reactivity differences depending on the atmosphere used (nitrogen or carbon monoxide).

Under the phase-transfer conditions, the initial reaction in the organic phase likely involves either conversion of $M_3(CO)_{12}$ to $M_3(CO)_{11}^{-2}$ by the quaternary ammonium hydroxide[2] or attack by hydroxide ion at a metal carbonyl carbon to give the anion **1** bearing a hydroxycarbonyl ligand.[4] The latter type of complex is analogous to species obtained from the phase-transfer catalyzed reaction of group 6 metal carbonyls with hydroxide ion.[5] Loss of carbon dioxide from **1** would generate the trinuclear metal hydride **2** which is the key species in the iron reaction and may or may not be so in the case of ruthenium (species of higher nuclearity are also possible with ruthenium).[6]

$$M_3(CO)_{12} + R_4N^+OH^- \rightarrow \underset{\mathbf{1}}{R_4N^+M_3(CO)_{11}COOH^-} \xrightarrow[-CO_2]{} \underset{\mathbf{2}}{R_4N^+HM_3(CO)_{11}^-}$$

Let us consider the consequences of using methoxide instead of hydroxide ion in the iron and ruthenium carbonyl catalyzed reactions of nitro compounds. If $M_3(CO)_{11}^{2-}$ was still generated, then one would observe little that had not already been noted in

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Table I. Yields of Products Obtained from the Carbonylation of Nitroarenes Using $NaOCH_3$ and Either $Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$

				product yields,[a] %				
Ar in **5**	catalyst	reaction atm	conversion, %	**6**	**7**	**8**	**9**	**10**
p-ClC_6H_4	$Ru_3(CO)_{12}$	CO/H_2	95	59		30		11
	$Fe_3(CO)_{12}$	CO/H_2	90		35	16		13
p-$CH_3OC_6H_4$	$Ru_3(CO)_{12}$	CO/H_2	55	56		40		
	$Ru_3(CO)_{12}$	CO		31				
	$Fe_3(CO)_{12}$	CO/H_2	81		62		18	12
p-$CH_3C_6H_4$	$Ru_3(CO)_{12}$	CO/H_2	59	32		18		
	$Fe_3(CO)_{12}$	CO/H_2	48		39		32	
	$Fe_3(CO)_{12}$	CO/H_2	67[b]		36	15	16	
Ph	$Ru_3(CO)_{12}$	CO/H_2	59	69		8-10	5	
	$Ru_3(CO)_{12}$	CO	60[c]	29				
	$Fe_3(CO)_{12}$	CO/H_2	52		61	20	18	
p-$C_6H_5COC_6H_4$	$Ru_3(CO)_{12}$	CO/H_2	72[d]	52	3	8		
	$Fe_3(CO)_{12}$	CO/H_2	94	12	45	14	10	

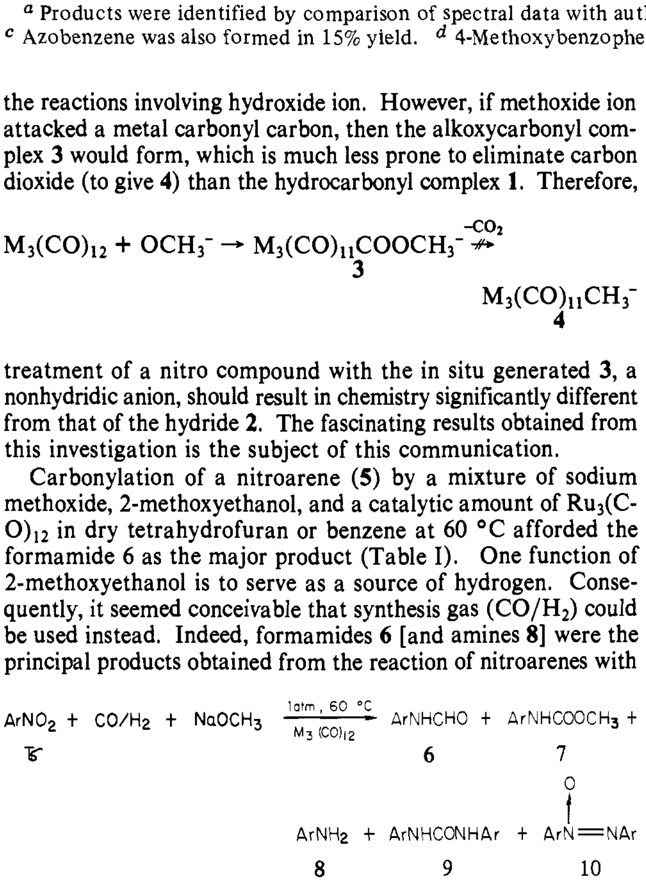
[a] Products were identified by comparison of spectral data with authentic materials. [b] Reaction was effected in the presence of 15-crown-5. [c] Azobenzene was also formed in 15% yield. [d] 4-Methoxybenzophenone was also found in 10% yield.

the reactions involving hydroxide ion. However, if methoxide ion attacked a metal carbonyl carbon, then the alkoxycarbonyl complex **3** would form, which is much less prone to eliminate carbon dioxide (to give **4**) than the hydrocarbonyl complex **1**. Therefore,

$$M_3(CO)_{12} + OCH_3^- \rightarrow \underset{\mathbf{3}}{M_3(CO)_{11}COOCH_3^-} \overset{-CO_2}{\not\rightarrow} \underset{\mathbf{4}}{M_3(CO)_{11}CH_3^-}$$

treatment of a nitro compound with the in situ generated **3**, a nonhydridic anion, should result in chemistry significantly different from that of the hydride **2**. The fascinating results obtained from this investigation is the subject of this communication.

Carbonylation of a nitroarene (**5**) by a mixture of sodium methoxide, 2-methoxyethanol, and a catalytic amount of $Ru_3(CO)_{12}$ in dry tetrahydrofuran or benzene at 60 °C afforded the formamide **6** as the major product (Table I). One function of 2-methoxyethanol is to serve as a source of hydrogen. Consequently, it seemed conceivable that synthesis gas (CO/H_2) could be used instead. Indeed, formamides **6** [and amines **8**] were the principal products obtained from the reaction of nitroarenes with CO/H_2 (1:1), $NaOCH_3$, and $Ru_3(CO)_{12}$ as the catalyst. Whichever way one effects this reaction ($2\text{-}CH_3OCH_2CH_2OH$ or CO/H_2), the use of methoxide instead of hydroxide ion has an important influence on the reduction process.



$$\underset{\mathbf{5}}{ArNO_2} + CO/H_2 + NaOCH_3 \xrightarrow[M_3(CO)_{12}]{1atm,\ 60\ ^\circ C} \underset{\mathbf{6}}{ArNHCHO} + \underset{\mathbf{7}}{ArNHCOOCH_3} + \underset{\mathbf{8}}{ArNH_2} + \underset{\mathbf{9}}{ArNHCONHAr} + \underset{\mathbf{10}}{Ar\overset{O}{\overset{\uparrow}{N}}{=}NAr}$$

Much more remarkable, however, is the effect of the *metal* of the catalyst on the reaction pathway. Substitution of $Fe_3(CO)_{12}$ for $Ru_3(CO)_{12}$ as the catalyst results in the formation of carbamate esters (**7**) as the major product, with ureas (**9**) as the main byproducts. With one low yield exception in each series, carbamate esters (or ureas) were not formed by using $Ru_3(CO)_{12}$ as the catalyst, and formamides were not obtained with $Fe_3(CO)_{12}$.

As indicated in Table I, the use of 15-crown-5 in the $Fe_3(CO)_{12}$ catalyzed reaction of *p*-nitrotoluene with CO/H_2 and $NaOCH_3$ resulted in increased conversion to products, but the yield of carbamate ester was not appreciably changed. The nitro compound was recovered when the substrate was exposed to CO/H_2 and $NaOCH_3$ in the absence of either $Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$.

It is premature to speculate on the mechanistic details of these reactions. However, the difference in behavior of the iron and ruthenium catalysts may be due to the facility of an intermediate such as **11** to undergo reductive elimination (and protonation) to give **7** or insertion of carbon monoxide into a metal–nitrogen bond,[7] followed by hydrogenation affording **6**.

$$\underset{\mathbf{3}}{M_3(CO)_{11}COOCH_3^-} \xrightarrow[-2CO_2]{RNO_2} \underset{\mathbf{11}}{(RN)M_3(CO)_9COOCH_3^-}$$

It is reasonable to ask whether the formamides and carbamate esters are formed from the corresponding amines, the latter produced by reduction of the nitro compounds as previously observed by phase-transfer catalysis. When *p*-toluidine was treated with $NaOCH_3$, CO/H_2, and *either* $Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$ as the catalyst, formamides were obtained in 68% (74% conversion) and 74% yields (77% conversion), respectively. Therefore, while it is conceivable that the $Ru_3(CO)_{12}$ catalyzed process proceeds via the amine, the $Fe_3(CO)_{12}$ catalyzed reaction clearly does not. It is also important to note that while ruthenium carbonyls are known to catalyze the carbonylation of heterocyclic secondary amines to formamides at moderate conversions (<50%), no carbonylation occurred in the case of aniline, an aromatic amine.[8] Furthermore, only aniline was isolated from the $Ru_3(CO)_{12}$ catalyzed reduction of nitrobenzene by 1:1 CO/H_2 at high temperatures (140–160 °C) and pressures (80–140 atm of CO) (diphenylurea was also formed by using high CO/H_2 ratios).[9] In addition, iron pentacarbonyl catalyzes the formylation of piperidine and cyclohexylamine under drastic conditions (200 °C, 95 atm).[10]

The following general procedure was used: a mixture of $Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$ (0.3 mmol) and sodium methoxide (6.0 mmol) in dry tetrahydrofuran (30–50 mL) was stirred under a carbon monoxide atmosphere for 3 h at room temperature. The nitro compound (4 mmol) in tetrahydrofuran (10 mL) was added, and the solution was then stirred overnight at 60 °C, under CO/H_2, at atmospheric pressure. The solvent was then removed by flash evaporation, and chromatography on silica gel afforded pure products.

In conclusion, nitro compounds can be converted to the industrially important formamides or carbamate esters, using simple iron and ruthenium clusters as catalysts, CO/H_2, and sodium methoxide. These reactions occur under exceedingly mild conditions and with good selectivity. Clearly, the metal as well as the methoxide ion have a very significant influence on the reaction pathway. Finally, metal carbonyl–alkoxide reactions should provide a rich chemistry in organic cluster[11] chemistry and may also prove of value in studies related to the water gas shift reaction.[5]

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