Catalytic Reduction of Nitrous Oxide to Dinitrogen by Carbon Monoxide using Group 8 Metal Carbonyl Anions†

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Metal carbonyls $[FeH(CO)_4]^-$, $[Fe_3(CO)_{11}]^{2-}$ and $[Ru_3(CO)_{12}]$ in the presence of KO_2CMe in dimethyl sulfoxide are effective catalyst systems for the reduction of N_2O to N_2 by CO. The observed catalytic activity for $[FeH(CO)_4]^-$ of 4.56 turnover number per h at 100 °C under a total pressure of less than 1 atm is the highest among the catalyst systems using KO_2CMe as the base. The kinetics of the reduction of N_2O by CO catalysed by the $[FeH(CO)_4]^-$–KO_2CMe system was investigated. A first-order dependence of the rate on both p_{N_2O} and the concentration of $[FeH(CO)_4]^-$ was established. The activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are 56.1 kJ mol^{-1} and −180 J K^{-1} mol^{-1}, respectively. The ion $[FeH(CO)_4]^-$ is converted into $[Fe_2(CO)_8]^{2-}$ during the course of catalysis. The reaction of $[Fe_2(CO)_8]^{2-}$ with N_2O yields 2.68 mol of N_2 and 1.38 mol of CO_2 per mol of the dinuclear species within 5 h at ambient temperature. This reaction is believed to be the process responsible for the catalytic reaction. A catalytic cycle including nucleophilic attack of $[Fe_2(CO)_8]^{2-}$ on N_2O to give a N_2O–Fe adduct, followed by an interligand oxygen transfer from the co-ordinated N_2O to CO to give N_2 and CO_2, is proposed to account for the observed catalysis. Another possible mechanism involving an electron transfer between $[Fe_2(CO)_8]^{2-}$ and N_2O as the first step is also discussed.

Nitrous oxide is a rather inert gas[1] and an extremely poor ligand.[2,3] To date, there is only one well characterized complex of N_2O which decomposes to give N_2O under mild conditions.[4,5] Compared to other nitrogen oxides, N_2O is much less reactive towards oxidation and reduction at room temperature. One of the few known reactions is its deoxygenation by transition-metal complexes.[1,2] A related catalytic oxidation of PPh_3 by N_2O using a cobalt(I) complex was also observed.[6]

The reduction of N_2O by carbon monoxide to dinitrogen [reaction (1)] does not proceed at an appreciable rate below

$$N_2O + CO \longrightarrow N_2 + CO_2 \qquad (1)$$

1000 K,[7] despite the fact that it is extremely thermodynamically favourable.[8] Heterogeneous systems are known to catalyse this environmentally important reaction typically at elevated temperature.[3,9] It is only recently that homogeneous catalysis of reaction (1) was first reported by us using a rhodium carbonyl compound in the presence of base.[8] The compound employed, $[Rh_2(CO)_4Cl_2]$, was converted into the catalytically active $[Rh(CO)_4]^-$. The reaction of $[Rh(CO)_4]^-$ with N_2O yielding N_2 and CO_2 simultaneously was responsible for the product formation. An electron-transfer mechanism was proposed. Isotopic labelling studies suggested that a direct oxygen transfer from co-ordinated N_2O to CO took place.

The success of rhodium carbonyl species in the catalysis of reaction (1) led us to examine the possibility of using other metal carbonyl anions as the catalyst systems. In this paper we report the results of studies on the catalytic activities for reaction (1) of carbonyl compounds of Group 8. These new catalyst systems appear to show activities greater than those of the cobalt family under the same reaction conditions.

Experimental

Materials.—The following compounds were obtained from the indicated suppliers: $[Fe(CO)_5]$, $[Ru_3(CO)_{12}]$ (Strem), KOH, KO_2CMe, dimethyl sulfoxide (dmso), dimethylformamide (dmf) (Merck), N_2O, CO and CH_4 (Matheson); dmso and dmf were dried over calcium hydride prior to use. The salts $[N(PPh_3)_2][FeH(CO)_4]$,[10] $[N(PPh_3)_2][Fe_3H(CO)_{11}]$,[11] $[N(PPh_3)_2]_2[Fe_3(CO)_{11}]$,[12] and $[N(PPh_3)_2]_2[Fe_4(CO)_{13}]$[13] were prepared as described in the literature.

General Procedure.—Infrared spectra were recorded on a Perkin-Elmer model 781 and a Bomem DA 3002 Fourier-transform spectrometer in 0.10 mm CaF_2 solution cells and EPR spectra on a Bruker 200D-SRC EPR instrument operated in the X band. A Varian Aerograph model 3700 gas chromatograph with a Shimadzu model Chromatopac C-R1B microprocessor was used for analysis of gas mixtures. A Pressure-Lok gas syringe obtained from Precision Sampling was employed for gas samplings. Separation of CO and N_2 was achieved on a molecular sieve 5A column, while a Porapak Q column was used to separate CH_4, CO_2 and N_2O. Helium was employed as the carrier gas for GC analysis and methane as the internal standard. Calibration plots of CO, CO_2 and N_2 were obtained according to procedures reported previously.[14,15] The reaction vessels were 24/40 single-neck round-bottom flasks (≈300 cm^3) connected *via* a side arm to a three-way stopcock. One stopcock lead was attached to a vacuum pump, and the other was used for addition of gases or stopped with a septum to allow gas sampling. A ground-glass adapter connected the vessel to a mercury manometer used to measure the initial partial pressure of each gas added. The reaction vessel was immersed in an oil to a fixed level. Both the solution and the oil-bath were stirred magnetically. A heating element connected *via* a contact thermometer to a mercury relay was employed to heat the system to a desired temperature.

Measurements of the Catalytic Activities of Various Metal Carbonyl Compounds.—A reaction vessel (305 cm^3) containing $[Ru_3(CO)_{12}]$ (4.77×10^{-5} mol), dmso (30 cm^3) and KO_2CMe (1.02×10^{-2} mol) was evacuated and charged with 360 Torr of CO and 350 Torr of N_2O. The system was heated with stirring at 100 °C for 7 h; the solution was cooled to room temperature and the gas mixture over the solution was sampled with a gas

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† *Non-SI units employed:* Torr ≈ 133 Pa, atm = 101 325 Pa.

Table 1 Results of the reduction of N_2O with CO catalysed by various metal carbonyls[a]

						Gas consumed		Gas produced		
Entry	Catalyst (mmol)	Solvent	Base	T/°C	t/h	CO(Torr)	N_2O(Torr)	CO_2(Torr)[b]	N_2(Torr)	Average rate/ turnovers h^{-1}
I	$[Rh(CO)_4]^-$ (0.106)	dmso	KOH	80	2	162	180	41	185	14.8
II	$[Ru_3(CO)_{12}]$ (0.0353)	dmso	KOH	80	2	261	219	0	217	16.8
III	(0.0477)	dmso	KO_2CMe	100	7	143	140	117(139)	145	2.15
IV	(0.0782)	dmso	KO_2CMe	80	7	192	191	129(160)	180	1.55
V	$[Os_3(CO)_{12}]$ (0.0477)	dmso	KO_2CMe	100	7	18	11	9(10)	16	0.25
VI	$[FeH(CO)_4]^-$ (0.143)	dmso	KO_2CMe	80	6	213	186	137(170)	169	2.79
VII	(0.143)	dmso	KO_2CMe	100	7	316	338	242(300)	322	4.56
VIII	(0.143)	dmf	KO_2CMe	80	7	80	85	67(83)	91	1.29
IX	(0.143)	dmf	—	100	10	203	206	162(201)	198	1.96
X	(0.143)	dmf	NEt_3	100	10	213	169	132(164)	173	1.71
XI	$[Fe_3(CO)_{11}]^{2-}$ (0.048)	dmso	KO_2CMe	80	6	137	112	87(108)	118	1.95
XII	$[Fe_3H(CO)_{11}]^-$ (0.048)	dmso	KO_2CMe	80	10	24	32	19(24)	28	0.28
XIII	$[Fe_4(CO)_{13}]^{2-}$ (0.036)	dmso	KO_2CMe	80	9	44	46	37(64)	51	0.57
XIV	$[Rh_2(CO)_4Cl_2]$ (0.154)	dmso	KO_2CMe	100	4	120	113	101	128	1.47

[a] See Experimental section for reaction conditions; $N(PPh_3)_2^+$ was the counter-cation whenever metal carbonyl anions were used. [b] Data in parentheses corrected for CO_2 produced after considering its solubility in the catalyst solution.

syringe and analysed by gas chromatography. The results indicated that 143 Torr of CO and 140 Torr of N_2O were consumed and 117 Torr of CO_2 and 145 Torr of N_2 were produced.

The activities of other metal carbonyls were measured by the same method and the results and detailed reaction conditions are presented in Table 1.

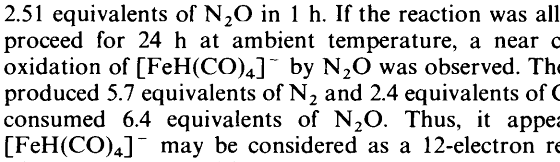
Kinetic Runs.—A reaction vessel (310 cm^3) containing $[N(PPh_3)_2][FeH(CO)_4]$ (1.43×10^{-4} mol), KO_2CMe (1.02×10^{-2} mol) and dmso (30 cm^3) was evacuated, charged with the desired pressures of CO, N_2O and a small amount of methane as an internal standard and then immersed in a preheated oil-bath. The solution was stirred magnetically at a constant spinning rate and the gas mixture over the solution was sampled and analysed periodically by gas chromatography. The results and detailed reaction conditions are presented in Table 2 and Figs. 1–3.

Results and Discussion

The catalysis of reaction (1) was typically carried out in a vessel (305 cm^3) containing 0.143 mmol of metal carbonyl, 1.00 g of base and 30 cm^3 of solvent under 350 Torr of N_2O and 360 Torr of CO at a temperature between 80 and 100 °C. The procedure for the catalytic reaction and the methods for analysing the gas components during the reaction follow those reported previously.[14,15] The detailed reaction conditions and the results obtained are presented in Table 1. Most runs in Table 1 were performed in the presence of KO_2CMe due to the fact that this base accelerates the catalysis, but does not irreversibly absorb CO_2 produced from the reaction. Surprisingly, the most active catalyst using this base is $[FeH(CO)_4]^-$ in dmso with a turnover number per h of 4.56 at 100 °C; $[Fe_3(CO)_{11}]^{2-}$ and $[Ru_3(CO)_{12}]$ exhibit activities of 1.95 turnover h^{-1} at 80 °C and 2.15 turnover h^{-1} at 100 °C, respectively. These activities are greater than that of the reported $[Rh_2(CO)_4Cl_2]$–KO_2CMe system which is 1.47 turnovers h^{-1} at 100 °C.[8] It should be noted that the comparison of the activities of various metal carbonyls is based on the number of moles of N_2 produced per mol of metal atom per hour. Other metal carbonyls that are less active include $[Os_3(CO)_{12}]$, $[Fe_3H(CO)_{11}]^-$ and $[Fe_4(CO)_{13}]^{2-}$. Although $[Rh(CO)_4]^-$ is known to be the active species in the $[Rh_2(CO)_4Cl_2]$–KO_2CMe system, the closely related $[Co(CO)_4]^-$ and $[Ir(CO)_4]^-$ show essentially no activity for reaction (1) under the same conditions. The results in Table 1 reveal that the activities of iron carbonyl anions lie in the following order $[FeH(CO)_4]^- > [Fe_3(CO)_{11}]^{2-} \gg [Fe_4(CO)_{13}]^{2-} > [Fe_3H(CO)_{11}]^-$. In dmso in the presence of KOH, $[Ru_3(CO)_{12}]$ shows activity comparable to that of $[Rh(CO)_4]^-$, while $[Co(CO)_4]^-$, $[Ir(CO)_4]^-$ and $[Os_3(CO)_{12}]$ are essentially inactive, and all iron carbonyl anions decompose under the reaction conditions.

Identification of Catalytic Intermediates.—In order to understand the mechanism of the catalytic reaction, attempts were made to identify the active catalyst intermediates by examining the catalyst solution using spectroscopic methods. A small portion of the reaction solutions during the course of catalysis was withdrawn periodically and immediately analysed by Fourier-transform infrared spectroscopy. For the catalysis of reaction (1) using $[N(PPh_3)_2][FeH(CO)_4]$, $[FeH(CO)_4]^-$ (1910m and 1880vs cm^{-1}) was rapidly converted into $[Fe_2(CO)_8]^{2-}$ (1910s and 1860s cm^{-1})[16] in 10 min at the beginning of the catalysis and remained the same to the end of the reaction. Interestingly, when $[N(PPh_3)_2][Fe_3(CO)_{11}]$ was used as the catalyst precursor, the dianion was also converted into $[Fe_2(CO)_8]^{2-}$ during the course of the catalysis of reaction (1). In the $[Ru_3(CO)_{12}]$–KO_2CMe system, $[Ru_3(CO)_{12}]$ was converted into $[Ru_4(CO)_{13}]^{2-}$ dianion (1950s and 1900s cm^{-1})[17] during the catalytic reaction.

Reaction of N_2O *with Iron Carbonyl Anions.*—Measurements of the reactivities of N_2O toward various metal carbonyl anions also help to understand the nature of the catalysis of reaction (1). In the absence of CO, $[N(PPh_3)_2][FeH(CO)_4]$ in dmso reacted with N_2O at ambient temperature to produce 2.46 equivalents of N_2 and 0.91 equivalents of CO_2 and consumed 2.51 equivalents of N_2O in 1 h. If the reaction was allowed to proceed for 24 h at ambient temperature, a near complete oxidation of $[FeH(CO)_4]^-$ by N_2O was observed. The system produced 5.7 equivalents of N_2 and 2.4 equivalents of CO_2 and consumed 6.4 equivalents of N_2O. Thus, it appears that $[FeH(CO)_4]^-$ may be considered as a 12-electron reductant which can react with $6N_2O$ to give $6N_2$ and $4CO_2$ as summarised in equation (2).



$$[FeH(CO)_4]^- + 6N_2O \longrightarrow 6N_2 + \underbrace{4CO_2 + FeO + OH^-}_{3CO_2 + HCO_3^-} \quad (2)$$

During the course of the reaction of $[FeH(CO)_4]^-$ with N_2O, $[Fe_3(CO)_{11}]^{2-}$ was observed as an intermediate product which reacted further with N_2O to yield N_2 and CO_2. The reaction of

Table 2 Effect of p_{N_2O}, p_{CO}, $[FeH(CO)_4^-]$[a] and temperature on the catalytic rate[b]

Run	10^3 $[FeH(CO)_4^-]$/mol dm^{-3}	p_{N_2O}/Torr	p_{CO}/Torr	T[b]/°C	10^5 k_{obs}[c]/s^{-1}
(*a*)	4.77	320	458	85	2.22 ± 0.03
(*b*)	4.77	231	460	85	2.28 ± 0.02
(*c*)	4.77	126	456	85	2.33 ± 0.03
(*d*)	4.77	268	502	85	2.20 ± 0.02
(*e*)	4.77	272	353	85	2.27 ± 0.05
(*f*)	1.67	192	472	100.5	1.72 ± 0.03
(*g*)	3.17	204	460	100.5	3.17 ± 0.05
(*h*)	4.77	193	452	100.5	5.08 ± 0.04
(*i*)	6.67	193	462	100.5	7.17 ± 0.04
(*j*)	8.33	197	465	100.5	9.75 ± 0.06
(*k*)	4.77	194	493	100	5.08 ± 0.01
(*l*)	4.77	210	488	92	3.13 ± 0.02
(*m*)	4.77	203	490	85	2.27 ± 0.01
(*n*)	4.77	200	510	75	1.29 ± 0.01

[a] The salt $[N(PPh_3)_2][FeH(CO)_4^-]$ was used. [b] The reaction conditions were described in the Experimental section; methane was used as the internal standard. Temperature deviation ±0.3 °C. [c] The estimated errors for k_{obs} are listed as standard deviations from linear regressions; a 3% error is estimated for each gas pressure measured.

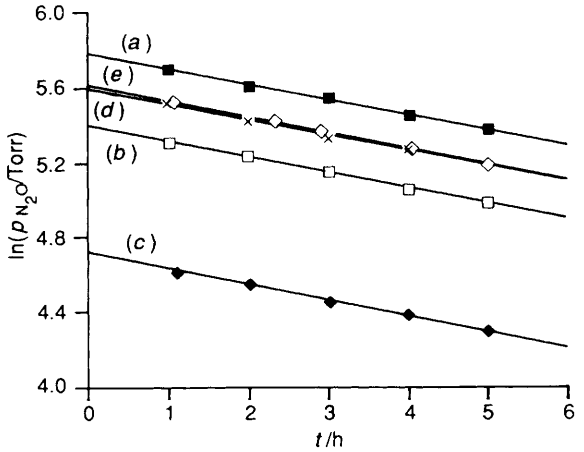


Fig. 1 Effect of the partial pressures of N_2O and CO on the rate of disappearance of N_2O; plots for runs (*a*)–(*e*) in Table 2

$[Fe_3(CO)_{11}]^{2-}$ with N_2O (1 atm) give 0.45 equivalent of N_2 and 0.058 equivalent of CO_2 in 15 h at room temperature. This reaction is much slower than that of $[FeH(CO)_4]^-$ with N_2O. It is interesting that, in the presence of CO, $[Fe_3(CO)_{11}]^{2-}$ is reduced to $[Fe_2(CO)_8]^{2-}$ which was not further reduced by CO under the reaction conditions. The latter species also reacts with N_2O to give 2.68 mol of N_2 and 1.38 mol of CO_2 per mol of the dinuclear species within 5 h at ambient temperature. From these studies it appears that the reactivities of iron carbonyl anions toward N_2O and their catalytic activities for reaction (1) follow the same trend, *i.e.* $[FeH(CO)_4]^- > [Fe_2(CO)_8]^{2-} > [Fe_3(CO)_{11}]^{2-}$.

Kinetic Investigations.—The catalysis of reaction (1) using $[N(PPh_3)_2][FeH(CO)_4]$–KO_2CMe was chosen for kinetic investigations to gain further understanding of the mechanism of the catalytic reaction. These studies were performed by measuring the rate of disappearance of N_2O. The gas mixture over the catalytic solution was periodically sampled and analysed by gas chromatography. Peak areas were converted into partial pressures by using calibration plots and corrected to their values at 27 °C by employing methane as the internal standard.

Effect of N_2O *and* CO *partial pressures.* The dependence of the catalytic rate on the partial pressure of N_2O was studied by using solutions containing $[N(PPh_3)_2][Fe(CO)_4]$ (4.77×10^{-3} mol dm^{-3}), KO_2CMe (0.340 mol dm^{-3}) and dmso (30.0 cm^3). While the initial partial pressure of N_2O was varied from 320 to 126 Torr, a constant CO pressure of 458 ± 2 Torr was employed. The detailed reaction conditions are listed in Table 2. As depicted in Fig. 1, plots of ln p_{N_2O} *vs.* time were linear for runs (*a*)–(*c*). These results indicate that the catalytic rate is first order in the partial pressure of N_2O. Further support of this relation comes from the slopes of these lines which are virtually constant within experimental error. All the slopes were determined by least-squares fit of the data. Consequently, the rate of the observed catalysis may be expressed according to equation (3) where $k_{obs} = (2.28 \pm 0.05) \times 10^{-5}$ s^{-1} is the average slope of lines (*a*)–(*c*) in Fig. 1.

$$-dp_{N_2O}/dt = k_{obs}p_{N_2O} \qquad (3)$$

To determine the effect of the partial pressure of CO on the catalytic rate, two kinetic runs with the same initial N_2O pressure of 270 ± 2 Torr and an initial CO partial pressure of 502 Torr for run (*d*) and 353 Torr for run (*e*) were performed. Again, linear plots of ln p_{N_2O} *vs.* time were obtained. Moreover, the slopes are the same as those of runs (*a*)–(*c*) within experimental error (Table 2). These results strongly imply that the rate of catalysis is independent of the partial pressure of CO. We had found that it was necessary to keep the partial pressure of CO higher than that of the N_2O during the catalytic reaction. A slight decrease in the catalyst activity would result if the partial pressure of CO was lower than that of N_2O.

Effect of iron concentration. To establish the dependence of the catalytic rate on the concentration of the iron catalyst, solutions with $[FeH(CO)_4^-]$ varying from 1.67×10^{-3} to 8.33×10^{-3} mol dm^{-3} were employed for kinetic studies. Linear plots of ln p_{N_2O} *vs.* time with different slopes were observed. A plot of log (k_{obs}) *vs.* log$[FeH(CO)_4^-]$ is linear (Fig. 2) with a slope of 1.07 ± 0.04 indicative of a first-order dependence of the catalytic rate on the concentration of the iron catalyst. Thus, the rate law may be written as in equation (4) where $k = (4.78 \pm 0.10) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}.

$$-dp_{N_2O}/dt = k[FeH(CO)_4^-]\,p_{N_2O} \qquad (4)$$

Effect of temperature. The influence on the catalytic rate of changing the reaction temperature was investigated in the range 100–75 °C. The catalyst solutions were prepared in a way similar to those of runs (*a*)–(*c*). A plot of ln(k/T) as a function of $1/T$ yields a straight line (Fig. 3), from the slope and intercept of which the activation parameters were calculated using the Eyring equation: $\Delta H^\ddagger = 56.1$ kJ mol^{-1}, $\Delta S^\ddagger = -180$ J K^{-1} mol^{-1}, and $\Delta G_{298}{}^\ddagger = 110$ kJ mol^{-1}.

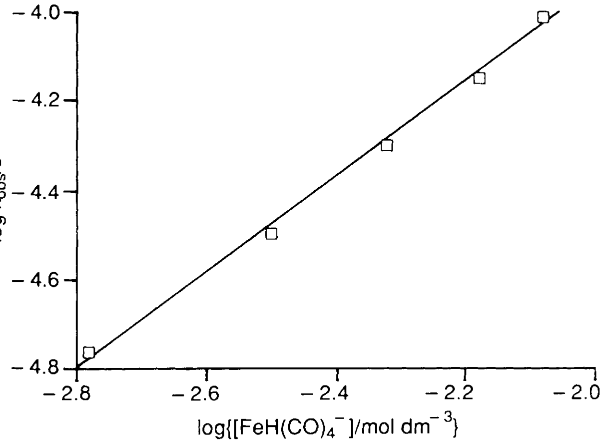


Fig. 2 Effect of $[FeH(CO)_4^-]$ on k_{obs}; plots for runs (*f*)–(*j*) in Table 2

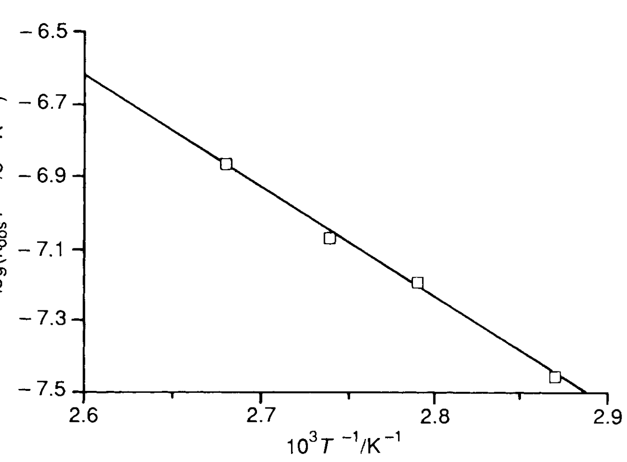


Fig. 3 Eyring plot of k_{obs} over the temperature range 75–100 °C for runs (*k*)–(*n*) in Table 2

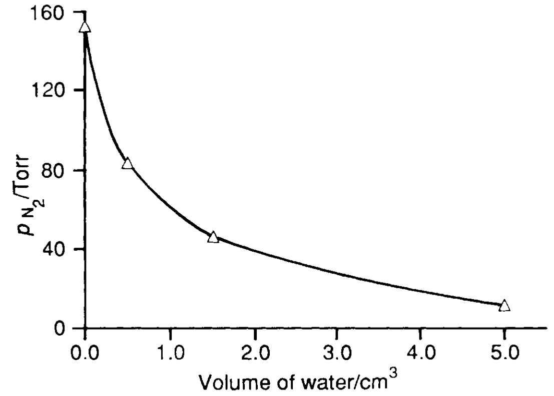


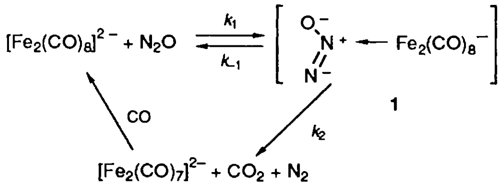
Fig. 4 Effect of water concentration on the rate of production of N_2. Reaction conditions: $[N(PPh_3)_2][FeH(CO)_4]$ (1.43 × 10^{-4} mol); KO_2CMe (5.1 × 10^{-3} mol); dmso (30 cm^3 − the amount of water added); CO (420 Torr), N_2O (390 Torr); temperature 81 ± 1 °C; reaction time 5 h

Effect of water and solvent. The dependence of the catalytic rate on the amount of water in the catalyst solutions was investigated by introducing varied amounts of water to catalyst solutions having the same compositions as those in run (*a*). The initial partial pressures of N_2O and CO were 390 and 420 Torr, respectively, and the reaction temperature was 81 ± 1 °C. Each run was allowed to proceed for 5 h before the reaction was terminated and cooled for GC analysis. A plot of the dinitrogen formation as a function of the water concentration in the catalyst solution is shown in Fig. 4. It is clear that the catalytic activity dramatically decreases as the amount of water increases.

The catalytic rate also depends greatly on the type of solvent used for the catalysis. In general, aprotic solvents, such as dmso and dmf gave higher catalytic rates than does a protic solvent. For example, the $[FeH(CO)_4]^-$–KO_2CMe system in dmso (entry VI of Table 1) produced 169 Torr of N_2 and 170 Torr of CO_2 in 6 h at 80 °C, while the same system in ethylene glycol gave only 3 Torr of N_2 and 3 Torr of CO_2 under the same conditions.

Catalytic Mechanism.—It is clear from the foregoing studies that iron carbonyl anions such as $[FeH(CO)_4]^-$, $[Fe_2(CO)_8]^{2-}$ and $[Fe_3(CO)_{11}]^{2-}$ are able to reduce N_2O to give N_2 and CO_2. Although their catalytic activities varied, these carbonyl anions are all effective catalyst systems for reaction (1). Moreover, they are all converted into $[Fe_2(CO)_8]^{2-}$ during the course of catalysis. Thus, it is reasonable to think that $[Fe_2(CO)_8]^{2-}$ is the catalytically active species responsible for the reduction of N_2O and CO_2. Under the catalytic conditions, $[FeH(CO)_4]^-$ is rapidly oxidized by N_2O to $[Fe_2(CO)_8]^{2-}$ in the presence of CO, while $[Fe_3(CO)_{11}]^{2-}$ is much less reactive toward N_2O, but is reduced more rapidly by CO to $[Fe_2(CO)_8]^{2-}$. As a result, both $[FeH(CO)_4]^-$ and $[Fe_3(CO)_{11}]^{2-}$ cannot be maintained at high concentration during the catalysis of reaction (1).

On the basis of the kinetic results, the fact that both N_2 and CO_2 are produced simultaneously and the assumption that $[Fe_2(CO)_8]^{2-}$ is the active species, the mechanism shown in Scheme 1 is proposed to account for the observed catalysis. This mechanism involves nucleophilic attack of the $[Fe_2(CO)_8]^{2-}$ anion at N_2O to give a N_2O–Fe adduct **1** as the first step. Interligand oxygen transfer from the co-ordinated N_2O to CO leads to the evolution of N_2 and CO_2 from the adduct. Finally, the resulting $[Fe_2(CO)_7]^{2-}$ picks up a free CO molecule to regenerate $[Fe_2(CO)_8]^{2-}$ and completes the catalytic cycle. If we view the co-ordinated N_2O in **1** as N_2O^{2-}, it is isoelectronic to a *N*-co-ordinated NO_2^-. The latter is known readily to transfer one of the oxygens to a bonded CO ligand.[18]



Scheme 1

During the course of catalysis a steady-state condition is established and all of the iron carbonyl species in the catalytic solution are present at a constant concentration. Application of the steady-state approximation to Scheme 1 leads to the rate law (5). Since $[Fe_2(CO)_8]^{2-}$ is the major species in the catalyst solution its concentration may be considered as half that of the initial iron carbonyl anion $[FeH(CO)_4]^-$. Thus, the rate law derived from Scheme 1 is completely consistent with the kinetic experiments which show that the rate of consumption of N_2O is first order in the iron concentration and first order in the partial pressure of N_2O. The rate law (5) as well as the kinetic results do not provide information on the rate-limiting step. Either the attack of $[Fe_2(CO)_8]^{2-}$ at N_2O or the decomposition of **1** to give N_2 and CO_2 is possible as the rate limiting step from the kinetic results. However, in view of the observation that the reactivities of iron carbonyl anion toward N_2O increase with

$$
\begin{aligned}
-\Delta p_{N_2O}/dt = k_2[\mathbf{1}] &= \frac{k_1k_2}{k_{-1}+k_2}[Fe_2(CO)_8{}^{2-}]p_{N_2O} \\
&= k'[Fe_2(CO)_8{}^{2-}]p_{N_2O} \\
&= k[FeH(CO)_4{}^-]p_{N_2O} \qquad (5)
\end{aligned}
$$

increasing negative charge on the metal centre, the rate-limiting step is likely to be nucleophilic attack of $[Fe_2(CO)_8]^{2-}$ at N_2O.

Although the present kinetic results are similar to those for the rhodium-catalysed reaction,[8] the catalytic mechanisms proposed for these two systems are quite different. An electron-transfer between $[Rh(CO)_4]^-$ and N_2O was proposed as the first step for the rhodium-catalysed reaction, while a nucleophilic attack of $[Fe_2(CO)_8]^{2-}$ at N_2O was the first step for the catalysis by iron carbonyl anions. There are two reasons which lead us to propose the present none electron-transfer mechanism for the iron-catalysed reaction. First, in the reaction of N_2O with $[FeH(CO)_4]^-$ or $[Fe_2(CO)_8]^{2-}$ we were unable to detect any iron–N_2O radical anion as was observed in the reaction of N_2O with $[Rh(CO)_4]^-$. Furthermore, unlike the catalysis with the rhodium system which requires both the presence of $[Rh(CO)_4]^-$ and $[Rh_4(CO)_{11}]^{2-}$, the catalysis of reaction (1) in the presence of $[Fe_2(CO)_8]^{2-}$ does not need other iron carbonyl anions as cocatalyst.

The large negative entropy of activation 180 J K^{-1} mol^{-1} is surprising, but may be understood based on the proposed mechanism. In Scheme 1 those steps which effect the rate law of the observed catalysis include the dissolution of gaseous N_2O, the co-ordination of N_2O to $[Fe_2(CO)_8]^{2-}$ giving a charge-separated N_2O–Fe adduct, and the oxygen transfer from co-ordinated N_2O to CO. These rate-limiting steps are all greatly entropy-decreasing reactions. It is clear from equation (5) that the observed total entropy results from a combination of these steps, although the contribution of each step to the total entropy cannot be determined at the present time. Homogeneous catalysis involving the transfer of gaseous substrates to the catalytic solutions in the rate-limiting steps generally has a large negative entropy of activation.[8,15]

Conclusion

It seems that carbonyl anions with sufficient electron density on the metal centres are vital for the carbonyl species to be effective in the catalysis of reaction (1). The observation that $[Rh(CO)_4]^-$, $[Fe_2(CO)_8]^{2-}$ and likely $[Ru_4(CO)_{13}]^{2-}$ are the anions responsible for the N_2O reduction in the corresponding metal carbonyl systems demonstrates that the catalytically active species for reaction (1) may be either mononuclear or cluster anions. For the $[FeH(CO)_4]^-$–KO_2CMe and $[Fe_3(CO)_{11}]^{2-}$–KO_2CMe systems the anions were converted into $[Fe_2(CO)_8]^{2-}$ during the course of catalysis. The kinetics of the $[FeH(CO)_4]^-$–KO_2CMe and the reported $[Rh(CO)_4]^-$ systems are similar, being first order in the concentration of metal and first order in the partial pressure of N_2O. A simple nucleophilic attack of $[Fe_2(CO)_8]^{2-}$ at N_2O is proposed to account for the observed kinetics. Finally, metal carbonyls of the iron family generally appear to be more active than those of the cobalt family.

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