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THE KINETICS OF THE ^{15}NO EXCHANGE WITH TRANSITION METAL NITROSYLS

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Summary

The kinetics of the ^{15}NO exchange with $M(NO)_2IL$ [M = Fe or Co, L = $P(C_6H_5)_3$ or $As(C_6H_5)_3$] in toluene have been studied, and the activation parameters evaluated. The effects of the ligands, L, on the rate constants indicate that the nitrosyl group behaves in much the same way as the CO group of carbonylic complexes.

Introduction

The reactions of transition metal carbonyls have been the subject of several investigations [1]. A substantial body of information is available on the kinetics of isotopic exchanges and of substitution reactions, mainly involving reactions of the CO group. First order kinetics are more frequently observed, but second order processes operate in some cases. Simultaneous first and second order processes have also been observed; presumably this behaviour would be commonly found unless the experimental conditions were such as to favour only one of the two parallel paths. An example of this is the exchange between solutions and gaseous CO, where the CO concentration in the liquid is limited by the gas solubility, and this can prevent observation of second order pathways.

Ligand exchange kinetics may indicate the reaction of one ligand without interference by other ligands, and so reveal possible non equivalence of apparently identical groups of the substrate. A difference in the rates of axial vs. radial CO groups exchange for $Mn(CO)_5Br$ is now well established [2] after several disputes [3 - 6]; similar behaviour is found for $Cr(CO)_4$·Phenanthroline [7].

Two techniques have been used to measure the rates of exchange of CO with metal carbonyls in solution: they involve measurement either of the decrease in the concentration of labelled CO in the gaseous phase [8], or of the variation of the isotopic composition of the complex in solution [9]. In some cases the results by the two methods do not agree; this has been ascribed to the volatility of the complex [9,10], but the issue is not definitely settled [11].

The reactions of the NO group in nitrosyl complexes have been much less investigated [12,13], even though the complexed NO group affords interesting variations of electronic and geometrical configuration. In amplification of a preliminary note [13], this paper presents the results of kinetic studies of ^{15}NO exchange with complexes of the type $M(NO)_2IL$ [$M = Fe$ or Co, $L = P(C_6H_5)_3$ or $As(C_6H_5)_3$]. The object of the study was to give information about the reactivity of the nitrosyl group[*] and about the influence of the paramagnetism of the iron complexes on the reaction mechanism.

Experimental

The method of measuring the NO exchange rate has been previously described [13]. The stability of the compounds was checked by recording the IR spectra of the solutions before and after the kinetic runs. Rate constants from duplicate measurements agreed within 15%. The solubility of NO in toluene was measured by Calderazzo and Cotton's method [14]. The Bunsen coefficients (α) at 25°, 16° and 1° were found to be 0.251, 0.278, and 0.315 respectively. Data for other temperatures were obtained from a plot of log α vs. $1/T$. The samples were prepared and purified by published procedures [15].

Results and discussion

Table 1 gives the results for the ^{15}NO exchange reactions with $M(NO)_2IL$. Previous exchange rate data [13] for $Co(NO)_2I[P(C_6H_5)_3]$, also included, are somewhat lower than the present ones; no certain explanation for this discrepancy can be offered, but reproducibility of the present results, even with samples of different origin, indicates their greater reliability. The NO concentration in solution ranged from about 0.2 to 2.5×10^{-3} mole·l^{-1}, to meet the requirements of intense signals in the mass spectrometer and of measurable variations of the $^{15}NO/^{14}NO$ ratio in the gaseous phase during runs. The substrate concentration was such as to ensure isotopic equilibration in between 30 and 180 min.

The data in Table 1 indicate that $Co(NO)_2I[P(C_6H_5)_3$ exchanges with NO follow the rate law

$v = k_{I} \cdot [\text{complex}]$

the iron derivatives $Fe(NO)_2IL$ follow the law

$v = k_{II} \cdot [\text{complex}] \cdot [NO]$,

and the $Co(NO)_2I[As(C_6H_5)_3]$ compounds the rate law

$v = k_{I} \cdot [\text{complex}] + k_{II} \cdot [\text{complex}] \cdot [NO]$

For the last complex the plot of $k_{I}^{obs}(0.5^{\circ})$ vs. [NO] is linear, with a non zero intercept on the k axis. Average values of k_{I} and k_{II} together with the available activation parameters are shown in Table 2. A second order path for $Co(NO)_2I[P(C_6H_5)_3]$ was probably not observed because of the low concen-

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[*] The study is currently being extended to other nitrosyl complexes containing linear and/or bent NO groups.

TABLE 1

KINETIC DATA FOR ^{15}NO EXCHANGE WITH $M(NO)_2IL$ IN TOLUENE

	Temp. (°C)	10^3 [compl.] (mole l^{-1})	10^3 [NO] (mole l^{-1})	10^3 k_I^{obs} (sec^{-1})	k_{II}^{obs} (l $mole^{-1}$ sec^{-1})
$Co(NO)_2I(PPh_3)$	25	4.55	0.156	0.61	3.92
		5.92	0.284	0.49	1.75
		5.92	0.410	0.53	1.29
		5.92	0.492	0.75	1.51
		10.4	11.7	0.97	0.08
		6.36	0.52	1.09	2.1
		5.96	0.8	1.26	1.6
		6.23	1.18	1.18	1.0
		6.50	1.5	1.20	0.8
		6.23	1.84	0.9	0.49
		12.9	10.6	1.22	0.115
	15	5.84	0.25	0.335	1.34
		6.30	0.32	0.30	0.94
		6.05	0.44	0.37	0.84
		5.84	0.45	0.45	1.0
		5.60	1.08	0.48	0.44
		5.90	1.38	0.38	0.27
	1	3.38	0.57	0.09	0.158
		3.38	0.61	0.10	0.164
	−16	5.90	0.52	0.018	0.034
$Co(NO)_2I(AsPh_3)$	0.5	3.46	0.17	0.97	5.7
		3.46	0.225	1.54	6.85
		5.67	0.31	1.25	4.03
		9.10	0.512	1.62	3.15
		6.84	0.52	1.70	3.27
		5.42	1.18	3.70	3.14
	15	3.99	0.18	1.62	8.9
		3.99	0.45	3.62	8.5
$Fe(NO)_2I(PPh_3)$	5	0.619	0.27	12.6	45.7
		0.639	0.31	17.0	50
		0.55	0.51	17.0	33
	0	5.92	0.355	6.9	19.4
		10.90	0.456	8.3	18.2
		5.9	0.46	9.3	20.2
		5.53	0.59	11.6	19.2
	−16	5.35	0.288	1.12	3.88
		5.35	0.29	1.60	5.5
		5.35	0.463	2.52	5.45
		5.42	0.873	3.8	4.35
		5.47	0.99	2.6	2.62
		5.16	2.50	6.95	2.77
		5.35	2.98	14.2	4.68
$Fe(NO)_2I(AsPh_3)$	0	2.27	0.478	11.0	23.2
		2.58	0.516	15.4	30.0
		2.27	0.62	13.2	21.4
	−12	5.24	0.445	4.15	9.3
	−17	3.63	0.182	0.72	4.0
		3.63	0.31	1.0	3.56
		11.6	0.61	2.75	4.52
		0.276	0.735	5.1	6.9

tration of NO necessary to give reliable kinetic data. Two parallel reaction pathways will be observed only if the two overall exchange rates are comparable; e.g. this is the case in the reaction at 0.5° for $Co(NO)_2As(C_6H_5)_3$, for which the two rates are almost equal. It follows that in this kind of reaction, involving a gaseous entering ligand, simultaneous first and second order pathways will be observed only if the ratio k_{II}/k_I is greater than about 10^3. To our

TABLE 2

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE EXCHANGE BETWEEN ^{15}NO AND M(NO)$_2$IL

	Temp. (°C)	$10^3\ k_I$	k_{II}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
$Co(NO)_2IPPh_3$	25	1.14			
	15	0.38		15.7	−19.5
	1	0.095			
	−16	0.018			
$Co(NO)_2IAsPh_3$	0.5	0.55	2.64		
$Fe(NO)_2IPPh_3$	5		42.9		
	0		19.4	14.0	−0.4
	−16		4.2		
$Fe(NO)_2IAsPh_3$	0		24.8		
	−12		9.3	12.5	−6.0
	−17		4.7		

knowledge this is the case in all the reported kinetic studies involving a gaseous reagent and a solution of a transition metal complex [11,16,17].

The data in Table 2 show that the nitrosyl group in these complexes behaves very much as does the CO group of carbonyl complexes. The results can be readily accounted for in terms of the σ donor ability of the ligand L and its influence on π bonding between the central metal and the NO group. On going from $P(C_6H_5)_3$ to $As(C_6H_5)_3$, the σ donor ability decreases, so favouring the nucleophilic attack of the entering NO in the second order path. On the other hand, the decrease of the electronic charge density at the central metal reduces the π bonding contribution to the metal—nitrosyl bonds and favours the detachment of the NO group in the first order process. Similar situations occur in reactions between carbonyl complexes and CO [11,16].

The low value of $\Delta H^{\ddagger}$ and the negative $\Delta S^{\ddagger}$ found for $Co(NO)_2I[P(C_6H_5)_3]$ suggest active participation of the solvent in the exchange process; the data for the other complexes indicate a simple associative mechanism for the second order reactions.

No definite influence of the paramagnetism is observed in these systems. The iron complexes exchange NO faster than the cobalt complexes, and only a second order process is found. Possibly the electron deficiency of the iron complexes favours the formation of a pentacoordinated, diamagnetic intermediate. However, the observed effect is small, and might arise simply from the variation of the central metal.

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