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NOTE

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^{15}NO EXCHANGE REACTIONS IN SOLUTION WITH $Co(NO)_2I[P(C_6H_5)_3]$

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A recent report by Palocsay and Rund[1] on the ^{15}NO exchange in the gas phase with the parent nitrosyls $Co(CO)_3NO$, $Fe(CO)_2(NO)_2$ and C_5H_5NiNO prompts us to present parallel data from this laboratory on the ^{15}NO exchange in solution with $Co(NO)_2I[P(C_6H_5)_3]$. Study of this type of exchange

(*a*) enlarges the scope of investigations of ligand exchanges involving different isotopic species and different experimental conditions (compare the work on the CO exchanges which have been followed in the gas phase and in solution by using ^{14}CO and $C^{18}O$ isotopic species analyzed respectively with radiochemical[2] and IR[3] methods*); which may permit generalizations about the kinetics which are not confined to the specific experimental conditions;

(*b*) provides information on the reactivity of the NO ligand in nitrosyl substrates, where it can be formally present in a variety of electronic situations[4], from NO^+ to NO^-.

Good kinetic runs were obtained throughout, and these obeyed McKay's equation[2] up to about 90% exchange; the linearity of the ln $A_0-A_\infty/A_t-A_\infty$ *vs.* t plots and the fact that the experimental A_∞ values agreed with those expected for two exchangeable NO ligands, confirmed the equivalence of both nitrosyl ligands. The reproducibility was satisfactory considering the sources of uncertainties of these measurements (see experimental part and ref. 2).

Some of the kinetic results are reported in Table 1. They indicate that the exchange is much faster than for $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$ in gaseous phase[1], and that, in contrast with the latter reactions, is first-order in substrate and zero-order with respect to the entering ligand. Preliminary ^{15}NO exchanges with $Co(CO)_3NO$ in toluene gave unreliable results, probably because of the slowness of the reaction.

Activation parameters are now being measured for the reactions described here and related exchanges, and the mechanistic and structural significance of our results will be discussed later.

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* Work is in progress (private communication from F. Basolo) on $N^{18}O$ exchange by IR method on substrates such as those studied in ref. 2.

TABLE 1

RATE DATA FOR THE ^{15}NO EXCHANGE WITH $Co(NO)_2I[P(C_6H_5)_3]$ IN TOLUENE AT 25°

$10^3 \times$ [compl] (mole·l^{-1})	$10^3 \times$ [NO] (mole·l^{-1})	$10^3 \times k_1^{obs}$ (sec^{-1})	k_2^{obs} (l·mole^{-1}·sec^{-1})
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
10.40	11.70	0.97	0.08

EXPERIMENTAL

Kinetic runs were performed as described in ref. 2, with toluene as solvent. The counter window was replaced by a connection to ampoules[*] from which gaseous samples could be taken for mass spectrometric analysis of the $^{14}NO/^{15}NO$ concn. ratio. No appreciable change of this ratio occurred in the time necessary to reach equilibrium in the Atlas CH-4 mass spectrometer. Toluene vapour was introduced into the mass spectrometer with argon and the NO sample. Argon, at atmospheric pressure, was also used to fill the circulating system. No correction at $m/e = 31$ was necessary, since the $^{15}NO^+$ peak was about one thousand times higher than $m/e = 31$ peak from toluene. To minimize memory effects half an hour was allowed between successive analyses.

The stability of $Co(NO)_2I[P(C_6H_5)_3]$ under the experimental conditions was checked by keeping a toluene solution of the complex in contact with unlabelled NO and observing that the intensities of the ν(NO) bands did not change during a time at least twice that used for the kinetic runs. The addition of about 2% of oxygen to the circulating gas caused complete decomposition of the sample in about 10 min.

The NO solubility in toluene was determined with a method similar to that previously described[2] for CO, with use of the CH-4 mass spectrometer in place of the Geiger counter.

The ^{15}NO samples from ONIA (Toulouse) had about 33% ^{15}N content; $Co(NO)_2I[P(C_6H_5)_3]$ was prepared and purified according to Hieber and Heinicke[5]; it was identified by its IR, UV and mass spectra. Erba reagent grade toluene was purified according to Vogel[6] and presaturated with argon. For other experimental conditions see ref. 2.

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[*] The ratio of the volume of an ampoule to that of the total occupied by the gas phase, was about 1/100, so that no significant change in overall composition of the reacting system was caused by the sampling.

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