SOLVENT EFFECTS ON THE KINETICS OF THE EXCHANGE BETWEEN ^{14}CO AND $Co(CO)_2(NO)[P(C_6H_5)_3]$

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SUMMARY

$Co(CO)_2(NO)[P(C_6H_5)_3]$ undergoes carbon monoxide exchange in different solvents according to a two-term rate law. The second-order rate constants are little influenced by the solvent, while the first-order rate constants vary with its nucleophilicity and steric requirements.

The results are discussed in terms of a suggested reaction mechanism.

INTRODUCTION

Recently we reported kinetic studies of the isotopic exchange reaction

$$Co(CO)_2(NO)L + {}^{14}CO \rightleftarrows Co({}^{14}CO)_2(NO)L + CO$$
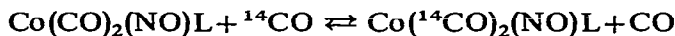
where $L = P(C_6H_5)_3$, $P(n-C_4H_9)_3$, $P(OC_6H_5)_3$ or $P(OCH_3)_3$. It was found that the reaction follows a two-term rate law of the type $v = k_1 \cdot [\text{complex}] + k_2 \cdot [\text{complex}] \cdot [CO]$, both steric and solvent effects being important in the first-order path[1]. An investigation on the study of the solvent effects seemed necessary to confirm the reaction mechanism.

This paper reports the study of the isotopic exchange reaction between Co-$(CO)_2(NO)[P(C_6H_5)_3]$ and radioactive carbon monoxide in a series of solvents of varying dielectric constant and basicity. Solvent effects are very small with metal carbonyl complexes because all the species involved in the reaction path are uncharged, but the study of solvent effects on reactions in which the electrostatic effect is absent can lead to clarification of the influence of other solvent properties on the reaction. Recent studies have been published on CO substitution[2-5], insertion[6,7], and isotopic exchange reactions[8]. In some cases the rate correlates with the dielectric constant[2,6], while in others it is influenced by the dielectric constant and also by the nucleophilicity of the solvent[3-5,7,8].

EXPERIMENTAL

Materials

The reagents and gases were prepared and/or purified as previously described[1]. Toluene was purified according to Vogel[9]. Carbon tetrachloride and acetonitrile

TABLE 1

RATE DATA FOR THE ^{14}CO EXCHANGE WITH $Co(CO)_2(NO)[P(C_6H_5)_3]$

Temp. (°C)	$10^2 \times [c]$ (M)	$10^4 \times [CO]$ (M)	$10^6 \times k_{I\ obs}$ (sec^{-1})
In bis(2-ethoxyethyl) ether			
53	1.0	69.6	15.0
53	1.0	69.6	16.1
53	1.0	69.6	15.4
53	1.0	6.8	1.1
53	1.0	6.8	1.0
53	1.0	3.4	0.7
53	1.0	2.5	0.3
60	2.5	62.0	15.0
60	3.2	62.0	19.0
60	0.9	9.4	2.8
60	0.9	3.7	2.0
In carbon tetrachloride			
53	1.1	59.2	17.3
53	1.1	59.2	17.0
53	1.1	59.2	16.9
53	1.5	5.2	1.8
53	1.1	5.2	1.5
53	1.5	3.1	0.9
60	1.0	52.3	22.4
60	2.4	52.3	21.0
60	1.0	5.9	3.0
60	1.0	5.9	3.8
60	1.0	3.4	1.2
In acetonitrile			
40	2.4	64.0	7.9
40	2.5	64.0	7.1
40	2.5	64.0	5.8
40	1.9	3.5	1.9
40	2.0	2.8	2.1
53	1.2	81.2	21.5
53	3.1	81.2	22.2
53	1.1	24.6	9.4
53	1.2	8.2	5.2
53	1.2	6.8	4.8
53	1.2	5.5	3.8
In dimethyl sulphoxide			
40	2.4	22.7	7.6
40	2.4	22.7	8.3
40	2.1	2.5	3.6
40	2.1	1.4	3.3
53	1.2	25.2	22.0
53	1.5	25.2	18.0
53	1.7	2.0	9.3
53	1.7	1.5	7.6

(continued)

TABLE 1 (continued)

Temp. ($^\circ$C)	$10^2 \times [c]$ (M)	$10^4 \times [CO]$ (M)	$10^6 \times k_{I\,obs}$ (sec^{-1})
In tetrahydrofuran			
53	1.5	444^a	19.8
53	1.3	444^a	21.4
53	1.2	444^a	22.3
53	1.0	44^a	3.1
53	1.1	40^a	2.6

^{a} CO partial pressure expressed in mm Hg (see experimental).

were purified by standard methods[10]. Tetrahydrofuran was refluxed over and distilled from potassium and benzophenone. Bis(2-ethoxyethyl) ether was distilled from lithium tetrahydridoalluminate in a nitrogen atmosphere[6]. Dimethyl sulphoxide was refluxed over CaH$_2$ and distilled under nitrogen[11]. All the solvents were carefully deoxygenated by flushing with argon or with carbon monoxide.

Kinetic measurements

The method used to investigate the rate of the ^{14}CO exchange with Co(CO)$_2$-(NO)[P(C$_6$H$_5$)$_3$] has been previously described[1]. The stability of the complex was checked in every solvent by measuring the IR and UV spectra of the solutions before and after the kinetic runs: in all cases there was no appreciable thermal decomposition nor any concentration change due to the solvent volatility. The extent of exchange followed ranged from 5 to 40%. The kinetic runs follow the McKay law[12] with good linear plots of log $(A_0 - A_\infty)/(A - A_\infty)$ vs. time (where A_0 is the initial radioactivity, A is the radioactivity at time t, and A_∞ is the radioactivity at equilibrium). The slopes of these plots give k_{app} which is related to the experimental rate constant k_{obs} by the equation:

$$k_{obs} = k_{app} \frac{x \cdot a^{1-\alpha} \cdot y \cdot b^{1-\beta}}{x \cdot a + y \cdot b} \tag{1}$$

where $a = [\text{complex}]$, $b = [CO]$ in the solution, $x = $ number of exchangeable CO's in the metal carbonyl, $y = $ ratio between the total number of CO molecules in the system and their number in the solution, $\alpha = $ reaction order with respect to the complex, $\beta = $ reaction order with respect to CO. The experimental first-order rate constant $(k_{I\,obs})$ was calculated assuming $\alpha = 1$ and $\beta = 0$. The rate constants were reproducible to within 15%. All the kinetic runs were performed in the dark.

Determination of the solubility of carbon monoxide

The solubility of CO in carbon tetrachloride[13] and in bis(2-ethoxyethyl) ether[6] is reported in the literature, and it was extrapolated or interpolated from these data. The determination in acetonitrile and dimethyl sulfoxide was made using the method of Calderazzo and Cotton with some modifications[6]. The thermostatted solvent was connected to vacuum for about 10 min while being stirred vigorously. The vacuum was then disconnected and the stirring continued for about 1 min to bring the vapour pressure to equilibrium. After that the flask was connected for a short time

TABLE 2.

RATE CONSTANTS AND THERMAL PARAMETERS FOR THE FIRST- AND SECOND-ORDER PROCESSES OF THE EXCHANGE REACTION

Solvent	Dielectric constant	Donor number[a]	Temp. (°C)	$10^7 \times k_1$ (sec^{-1})	$10^3 \times k_2$ (l·mole^{-1}·sec^{-1})	$\Delta H^{\ddagger}$ (kcal·mole^{-1})	$\Delta S^{\ddagger}$ (e.u.)
Bis(2-ethoxyethyl) ether	5.68[b]		53		2.2	6.1	−51 (2nd order)
			60		2.8	33.3	+9.5 (1st order)
Carbon tetrachloride	2.2[c]		53	2.0	2.8	10.7	−37.5 (2nd order)
			60	6.0	4.1	32.8	+10 (1st order)
Toluene[d]	2.34[c]		43.5	0.8	0.3	18.7	−17.4 (2nd order)
			52.8	3.4	0.7	9.3	−55.0 (1st order)
Acetonitrile	38.0[a]	14.1	40	18.0	0.8	15.9	−21.9 (2nd order)
			53	34.0	2.3		
Tetrahydrofuran	7.6[a]	20.0	53	11.8	e		
Dimethyl sulfoxide	45.0[a]	29.8	40	31.0	2.2	13.7	−40.1 (1st order)
			53	78.0	4.8	12.0	−32.0 (2nd order)

[a] From ref. 15. [b] From ref. 6. [c] Dielectric constants from National Bureau of Standards, Circular 514, 1953. [d] From ref. 1. [e] Can not be calculated as the CO concentration is not known.

to a gasometer filled with CO at atmospheric pressure, and then quickly to the gas buret. After the equilibrium had been reached, the buret was read, and from the quantity of CO adsorbed by the solvent the solubility was calculated. The method was checked first using toluene, since the solubility of CO in toluene is known[1]. The solubility, expressed as Bunsen coefficient, in acetonitrile was 0.182 ± 0.010 at $40°$ and 0.264 ± 0.013 at $53°$; in dimethyl sulfoxide it was 0.054 ± 0.004 at $40°$ and 0.060 ± 0.004 at $53°$, the results representing the average of four determinations in each case. The CO solubility was not determined in tetrahydrofuran owing to the high vapour pressure of this solvent. It was possible to determine k_1 in this solvent, by plotting $k_{1 obs}$ vs. the partial pressure of CO. A check with other solvents (acetonitrile, dimethyl sulfoxide, carbon tetrachloride) shows that k_1 obtained by this method is the same as that obtained by plotting $k_{1 obs}$ vs. the CO concentration. On the other hand, the knowledge of the CO concentration is not necessary to solve eqn. (1) as the product $y \cdot b$ is equal to the number of millimoles of CO in the enclosed system divided by the number of milliliters of solvent used[14].

RESULTS AND DISCUSSION

Table 1 gives the kinetic results for the isotopic exchange in bis(2-ethoxyethyl) ether, carbon tetrachloride, acetonitrile, dimethyl sulfoxide and tetrahydrofuran. The CO concentration was varied 10- to 20-fold, the concentration of complex being approximately 1×10^{-2} moles/l. The exchanges follow a two-term rate law, $v = (k_1 + k_2 \cdot [CO]) \cdot [complex]$, except with bis(2-ethoxyethyl) ether. Plotting the experimental first-order rate constant $k_{1 obs} = k_1 + k_2 \cdot [CO]$ vs. $[CO]$ generally gave

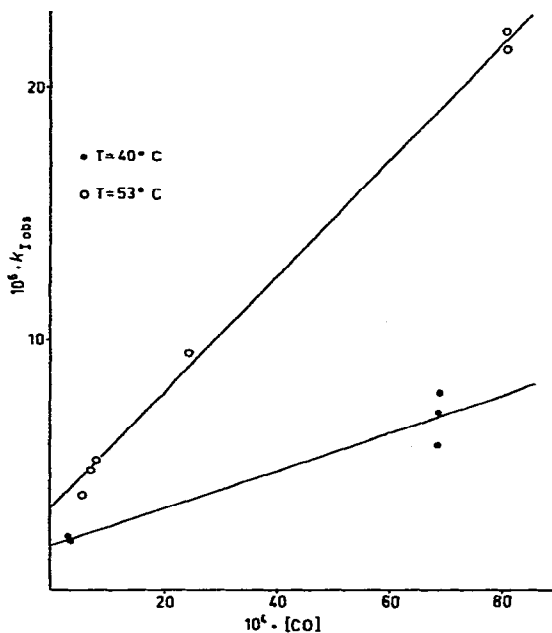Fig. 1. Plots of $k_{1 obs}$ vs. $[CO]$ at different temperatures for the exchange reaction $Co(CO)_2(NO)[P(C_6H_5)_3]$ $+ ^{14}CO$ in acetonitrile.

good linear plots (see Fig. 1), from which the rate constants k_1 and k_2 of the first- and second-order reaction paths were evaluated.

The rate constants and the corresponding thermal parameters are given in Table 2. It gives also the dielectric constant and the donor number[15] of the solvents. The donor number is considered a semiquantitative measure of the solvent–solute interactions, and represents the ability of the solvent to give complexes with the reference acceptor, $SbCl_5$, in dichloroethane.

The results in Table 2 show that the first-order rate constants remain small and almost constant in solvent of low nucleophilicity, but increase in solvents of high donor properties. It is in fact known that acetonitrile, dimethyl sulfoxide and tetrahydrofuran are coordinated in certain complexes, in which the solvent molecules are attached to the metal atoms[15]. These results agree with those found by Cardaci et al.[5] for the reaction of $Co(CO)_3NO$ with $As(C_6H_5)_3$ in different solvents, although these authors found greater differences in the rate constants.

Anomalous behaviour was found with bis(2-ethoxyethyl) ether and tetrahydrofuran. Bis(2-ethoxyethyl) ether has a moderate coordinating ability, but it does not influence the rate, because of the great steric hindrance of the molecule. Tetrahydrofuran has a high donor number but it does not increase the rate as much as acetonitrile and dimethyl sulphoxide because they have more favourable steric requirements[15]. Anomalous behaviour of the ethers has also been noticed in other cases[2b,5,6,8]. The results obtained show a large intervention of the solvent in the first-order path. As in other tetrahedral, pseudo-octahedral and octahedral complexes[5,16,7] it can be assumed that the first-order path is a solvent-assisted dissociative mechanism; however, as the differences in the activation parameters are great and the nature of the interaction is specific and markedly dependent on the properties of the solvent, an associative path with the solvent could also be present in some cases.

The second-order constants vary very little between the several solvents. The thermodynamic and kinetic data support a bimolecular displacement mechanism with nucleophilic attack by the CO ligand on the metal atom. The formation of the pentacoordinated reactive intermediate is slightly influenced by the nature of the solvent.

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