

## SOLVENT EFFECTS ON THE KINETICS OF THE MONOSUBSTITUTION REACTION OF $\text{Co}(\text{CO})_3\text{NO}$ WITH TRIPHENYLARSINE AND TRIPHENYLPHOSPHINE

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### SUMMARY

The kinetics of monosubstitution reactions of  $\text{Co}(\text{CO})_3\text{NO}$  with  $\text{As}(\text{C}_6\text{H}_5)_3$  and  $\text{P}(\text{C}_6\text{H}_5)_3$  in cyclohexane, toluene, nitromethane, tetrahydrofuran, acetonitrile and dimethylsulfoxide fit the two-term equation  $v = (k_1 + k' \cdot [\text{L}]) \cdot [\text{S}]$ , where L and S refer to the ligand and the substrate. The rate constant,  $k'$  for the second-order process (associative with the ligand) varies over a 5-fold range with the change in the dielectric constant of the solvent. The rate constant,  $k_1$ , for the first-order process changes by factor of less than 2 with the dielectric constant in the first three, non-coordinating, solvents, but in the latter three the variation is  $10^3$  times greater. This large increase is accounted for in terms of an associative intervention of the solvent in the first-order process. This interpretation is supported by the activation parameters, which are typical of a dissociative mechanism for the first three non coordinating solvents, while for the latter three they tend towards values typical of an associative mechanism.

### INTRODUCTION

Detailed kinetic studies have been made of ligand substitutions in neutral carbonyl and carbonylnitrosyl complexes, but little work has been reported on solvent effects. In  $\text{M}(\text{CO})_5\text{X}^1$ , and analogous complexes<sup>2,3</sup>, there is a small influence of solvent dielectric constant which depends on the difference in polarity between the activated complex and the initial state, but in other cases<sup>4-8</sup> the reaction mechanism is influenced by the coordinating power of the solvent.

The reaction between  $\text{Co}(\text{CO})_3\text{NO}$  and  $\text{As}(\text{C}_6\text{H}_5)_3$  has been studied to see if such solvent influences are general. It has previously been shown for this reaction that both dissociative and associative processes occur in benzene<sup>9</sup>, the relative weight of the separate reaction paths depending on the substrate and entering ligand used. Thus it might be possible to observe intervention by coordination of the solvent for both the dissociative and the associative mechanism. The results below show that, in fact, changing the donor solvent can divert the reaction from a dissociative path to an associative interaction with the solvent.

## EXPERIMENTAL

$\text{Co}(\text{CO})_3\text{NO}$  was prepared by Seel's method<sup>11</sup>. Triphenylarsine and triphenylphosphine were commercial products. The complexes  $\text{Co}(\text{CO})_2\text{NOAs}(\text{C}_6\text{H}_5)_3$  and  $\text{Co}(\text{CO})_2\text{NOP}(\text{C}_6\text{H}_5)_3$  were prepared as in ref. 10.

Solvents were freed from traces of water as follows: cyclohexane and toluene were distilled over Na; nitromethane was dried over  $\text{P}_2\text{O}_5$  and fractionated<sup>12</sup>; tetrahydrofuran (THF) was treated with KOH pellets in the presence of benzoquinone, and distilled over Na<sup>13</sup>; acetonitrile was treated as described by Coetree *et al.*<sup>14</sup> (method E); dimethylsulphoxide (DMSO) was refluxed over  $\text{CaH}_2$  and distilled under nitrogen<sup>15</sup>. All the solvents were carefully deoxygenated by nitrogen flushing since oxygen causes decomposition of  $\text{Co}(\text{CO})_3\text{NO}$  and its monosubstituted derivatives<sup>10,16</sup>. THF had to be fresh distilled before use to give reproducible kinetic data<sup>17</sup>.

The carbonylic and nitrosylic IR stretching bands of the monosubstituted complexes were affected differently from those of  $\text{Co}(\text{CO})_3\text{NO}$  on varying the solvent so we had to use different ways of following the reactions:

(a). In cyclohexane and toluene both the  $\nu(\text{CO})$  ( $A_1$ ) and  $\nu(\text{NO})$  bands of  $\text{Co}(\text{CO})_3\text{NO}$ , and the  $\nu(\text{CO})$  ( $A''$ ) and  $\nu(\text{NO})$  bands of the monosubstituted complexes were followed.

(b). In nitromethane and acetonitrile only the  $\nu(\text{CO})$  ( $A_1$ ) band of  $\text{Co}(\text{CO})_3\text{NO}$  was followed.

(c). In THF and DMSO the UV change of absorbancy at 4400 Å was followed.

For the IR measurements a Perkin-Elmer 337 Spectrophotometer with 0.1 or 0.5 mm NaCl cells was employed. The UV measurements were performed with an UV-VIS Hitachi Perkin-Elmer 139 Spectrophotometer and 0.5 cm quartz cells. The rate constants obtained from disappearing and appearing bands, in cyclohexane and toluene agreed satisfactorily. Runs were carried out in dark ampoules sealed under nitrogen. The reaction between  $\text{Co}(\text{CO})_3\text{NO}$  and  $\text{P}(\text{C}_6\text{H}_5)_3$  in DMSO was carried out in a thermostatted UV cell, because of the relatively high reaction rate at the concentrations used.

Under the conditions used reagents and reaction products were shown to be fairly stable for the times involved. Owing to the difficulty in obtaining good IR spectra in DMSO, the stability was checked by polarography<sup>18</sup>. Only in nitromethane did significant decomposition of the reagents and products occur during the reaction; the monosubstituted complex is less stable than  $\text{Co}(\text{CO})_3\text{NO}$  in this solvent, and the rates were measured only for the initial stages of the reaction; the data appeared only slightly less accurate than in the other case.

The absorbancies at the end of the reactions were derived from Beer's law plots of the reagents and products, performed in the different solvents, but in some cases they were checked by following the reactions to completion. Only in DMSO and nitromethane were the calculated values different from the experimental ones being slightly higher apparently because of a small amount of decomposition.

Except in DMSO, when the polarographic method was employed (see above), the final products were identified by their IR carbonylic and nitrosylic stretchings. These were as follows ( $\text{cm}^{-1}$ ) in the different solvents:

(a).  $\text{Co}(\text{CO})_3\text{NO}$ : cyclohexane  $\nu(\text{CO})$  ( $A_1$ ) 2100,  $\nu(\text{CO})$  ( $E$ ) 2034,  $\nu(\text{NO})$  1803; toluene 2104, 2033, 1807; nitromethane 2105, 2032, 1800; THF 2101, 2032, 1796; acetonitrile 2104, 2034, 1800.

(b).  $\text{Co}(\text{CO})_2(\text{NO})[\text{As}(\text{C}_6\text{H}_5)_3]$ : cyclohexane  $\nu(\text{CO}) (A')$  2036,  $\nu(\text{CO}) (A'')$  1979,  $\nu(\text{NO})$  1765; toluene 2036, 1980, 1763; nitromethane 2039, 1980, 1759; THF 2034, 1978, 1758; acetonitrile 2039, 1980, 1759.

(c).  $\text{Co}(\text{CO})_2(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]$ : acetonitrile  $\nu(\text{CO}) (A')$  2038,  $\nu(\text{CO}) (A'')$  1978,  $\nu(\text{NO})$  1752.

The experimental results fit the rate equation  $v = (k_1 + k' \cdot [\text{L}]) \cdot [\text{Co}(\text{CO})_3\text{NO}]$ , previously<sup>9</sup> obtained assuming a reaction mechanism with two parallel paths, first- and second-order respectively; where  $k_1$  is the rate constant for the first order process and  $k'$  that of the second-order process. The experimental values,  $k_1(\text{obs})$  and  $k_{11}(\text{obs})$  listed in the tables, are equal to  $(k_1 + k' \cdot [\text{L}])$  and  $(k_1/[\text{L}] + k')$ , respectively.

To provide activation parameters, reactions were performed at different temperatures. The temperature ranges varied with the solvent and the ligand within the interval 30–50°. The  $\lg k$  vs.  $1/T$  plots were all linear, and the uncertainty in values of  $\Delta E^\ddagger$  was  $\pm 1$  kcal/mole.

Reactions were followed to 10% completion in toluene and cyclohexane but to 80% completion in the other cases. The  $\text{Co}(\text{CO})_3\text{NO}$  concentration was about  $10^{-2}$  molar for the IR studies and about  $5 \cdot 10^{-3}$  molar for the UV studies. The ligand concentration was as far as possible, kept at least 10 times higher than that of the substrate. In some cases, however, in order to reveal any possible small first-order contribution to the rate the ratio was lowered to about 5.

## RESULTS AND DISCUSSION

The rate data are given in Tables 1 to 3. Table 4 shows the  $k_1$  and  $k'$  values, derived from the experimental values,  $k_1(\text{obs.})$  and  $k_{11}(\text{obs.})$  by use of literature data also. Table 5 compares the rate constants (extrapolated when necessary) and activation parameters for the reaction with  $\text{As}(\text{C}_6\text{H}_5)_3$  at 40° in different solvents.

In cyclohexane, toluene and nitromethane the  $k_{11}(\text{obs.})$  values of Table 1 for the reaction involving  $\text{As}(\text{C}_6\text{H}_5)_3$  depend linearly on  $1/[\text{L}]$  (see Fig. 1a). The non-zero intercept and the slope of the plots give, by application of the above two-term rate equation, the  $k'$  and  $k_1$  values of Table 4. In  $\text{CH}_3\text{CN}$  and DMSO the values of  $k_1(\text{obs.})$  do not vary with the ligand concentration (see Table 2 and Fig. 1b), while in THF the  $k_1(\text{obs.})$  values depend linearly on  $[\text{L}]$ , with a non-zero intercept. The corresponding  $k_1$  and  $k'$  values are given in Table 4.

For  $\text{P}(\text{C}_6\text{H}_5)_3$  in  $\text{CH}_3\text{CN}$  the  $k_{11}(\text{obs.})$  values are independent of the ligand concentration (see Table 3). In DMSO the  $k_1(\text{obs.})$  values are linear functions of  $[\text{L}]$  (see Table 3 and Fig. 1b). The non-zero intercept of this plot gives, as in benzene<sup>9</sup>, a  $k_1$  value coinciding with the corresponding value obtained for the reaction with  $\text{As}(\text{C}_6\text{H}_5)_3$ .

It seems likely that when  $k_1$  and  $k'$  values cannot be determined together, the reason probably lies in too great a difference between the contributions of the two parallel reaction paths. The relative contributions should be influenced both by the type of solvent and by the nucleophilicity of the entering ligand. The rate constants for the first-order path of the reaction with  $\text{As}(\text{C}_6\text{H}_5)_3$  in cyclohexane, toluene and nitromethane, agree with those found for the same reaction in benzene<sup>9</sup>, which indicates that the mechanism is purely dissociative. This is further supported by the agreement with the rate constants obtained for the  $\text{C}^{18}\text{O}$  exchange with the same substrate<sup>19</sup>.

TABLE I  
EXPERIMENTAL SECOND-ORDER RATE CONSTANTS  $k_{II}(\text{obs.})^a$  FOR THE MONOSUBSTITUTION REACTION  $\text{Co}(\text{CO})_3\text{NO} + \text{As}(\text{C}_6\text{H}_5)_3$  IN CYCLOHEXANE, TOLUENE AND NITROMETHANE

Temp. (°C)	In cyclohexane			In toluene			In nitromethane		
	$10^3 [\text{C}]$ (M)	$10^3 [\text{L}]$ (M)	$10^5 k_{II}(\text{obs.})$ (l·mole <sup>-1</sup> ·sec <sup>-1</sup> )	$10^2 [\text{C}]$ (M)	$10^2 [\text{L}]$ (M)	$10^4 k_{II}(\text{obs.})$ (l·mole <sup>-1</sup> ·sec <sup>-1</sup> )	$10^2 [\text{C}]$ (M)	$10 [\text{L}]$ (M)	$10^4 k_{II}(\text{obs.})$ (l·mole <sup>-1</sup> ·sec <sup>-1</sup> )
40.0	0.9723	4.902	1.91	0.9849	4.992	3.02			
		6.219	1.63		5.981	2.90			
		7.078	1.66		7.016	2.43			
		8.127	1.39		8.004	2.09			
		9.837	1.27		8.995	2.09			
		12.245	1.27		10.009	2.10			
		14.141	1.15		11.001	1.91			
45.0		16.549	1.09		12.021	1.93			
	0.9983	5.000	3.53	0.9948	5.003	6.10	2.06	1.068	1.07 <sup>b</sup>
		6.095	3.29		6.093	5.21	2.24	2.005	0.81 <sup>b</sup>
		6.987	2.81		6.968	4.92	2.08	3.310	0.75 <sup>b</sup>
		7.915	2.77		8.088	4.80	2.09	4.258	0.68 <sup>b</sup>
		10.069	2.45		9.230	3.98			
		12.108	2.07		10.490	3.81			
50.0		13.889	2.13		11.705	3.46			
		16.056	1.95		12.982	3.46			
	1.0705	4.817	7.19	1.0442	5.009	11.80	0.93	1.065	1.89
		5.892	6.58		5.972	9.86	1.96	2.092	1.35
		6.820	5.88		7.039	8.55	1.87	3.331	1.27
		8.209	4.97		9.000	7.33	2.36	4.180	1.09
		9.124	4.97		10.031	7.00			
	11.928	4.36		10.942	6.55				
	14.056	4.04		11.985	6.05				
	16.193	3.69							

<sup>a</sup> See rate eqn. in the text. <sup>b</sup> Values obtained at 44.7°.

TABLE 2

EXPERIMENTAL FIRST-ORDER RATE CONSTANTS  $k_1(\text{obs.})^a$  FOR THE MONOSUBSTITUTION REACTION  $\text{Co}(\text{CO})_3\text{NO} + \text{As}(\text{C}_6\text{H}_5)_3$  IN TETRAHYDROFURAN, ACETONITRILE AND DIMETHYLSULPHOXIDE

Temp. (°C)	$10^3$ [C] (M)	$10^2$ [L] (M)	$10^5 k_1(\text{obs.})$ ( $\text{sec}^{-1}$ )
<i>In tetrahydrofuran</i>			
40.0	5.35	5.286	1.97
	6.33	10.797	2.00
	5.02	20.520	2.21
45.0	4.85	29.680	2.37
	5.35	4.959	3.83
	5.05	10.960	3.80
	5.29	20.660	4.02
50.0	5.10	30.180	4.18
	4.87	6.190	6.90
	5.02	10.760	6.86
	5.04	15.900	7.30
	5.07	20.470	7.37
	4.76	30.090	6.98
	7.00	41.760	8.04
	5.30	47.750	7.82
	5.05	49.430	8.23
<i>In acetonitrile</i>			
30.0	17.90	7.885	1.39
	18.50	12.157	1.30
	20.25	16.503	1.43
35.5	15.50	4.997	2.50
	21.72	8.098	2.37
	15.25	12.052	2.68
40.0	19.25	16.047	2.36
	13.75	4.948	3.89
	17.60	6.005	3.74
	18.65	7.027	3.78
	16.75	8.001	4.02
	22.60	11.369	3.62
<i>In dimethylsulphoxide</i>			
30.0	1.59	5.494	11.5
	3.19	18.940	11.7
	2.86	50.210	14.8
35.0	4.15	2.449	22.5
	2.30	26.220	22.6
	2.55	49.400	23.1
40.0	5.80	5.122	43.9
	2.90	5.337	38.3
	2.66	26.760	43.2
	3.73	49.940	41.8
	2.87	50.090	40.8

<sup>a</sup> See rate eqn. in the text.

The  $k_1$  values in benzene, cyclohexane, toluene and nitromethane, and all the  $k'$  values change less than 5 times with change in the solvent dielectric constant. Such a relatively small variation may be interpreted as a normal dielectric effect on neutral

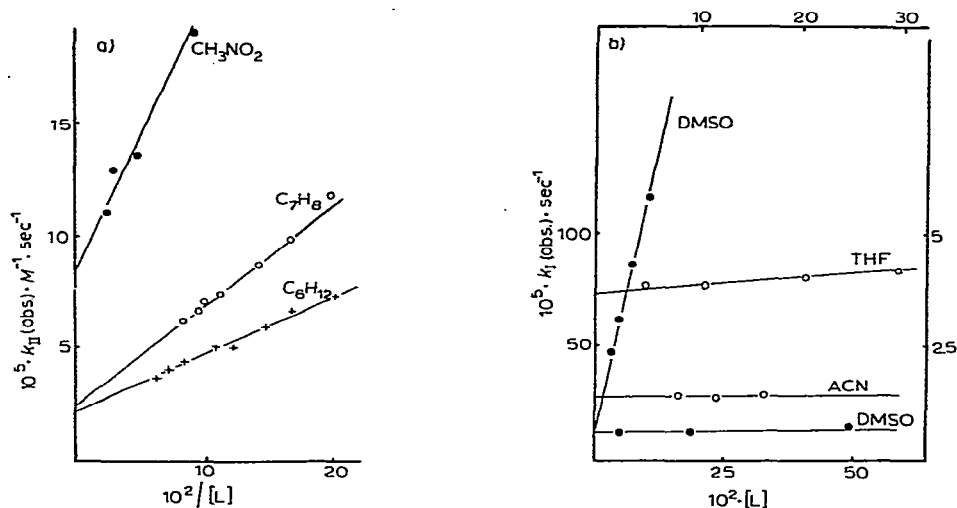


Fig. 1. (a).  $k_{II}$  (obs.) vs.  $1/[L]$  plots for the reaction with  $\text{As}(\text{C}_6\text{H}_5)_3$  in cyclohexane, toluene and nitromethane. (b).  $k_I$  (obs.) vs.  $[L]$  plots for the reaction with  $\text{As}(\text{C}_6\text{H}_5)_3$  in THF,  $\text{CH}_3\text{CN}$  and DMSO (flat curve), and with  $\text{P}(\text{C}_6\text{H}_5)_3$  in DMSO (steep curve); the left ordinate and the lower abscissa refer to DMSO, the right ordinate and the higher abscissa to THF and  $\text{CH}_3\text{CN}$ .

TABLE 3

EXPERIMENTAL FIRST- AND SECOND-ORDER RATE CONSTANTS  $k_I(\text{obs.})^a$  AND  $k_{II}(\text{obs.})^a$  FOR THE MONOSUBSTITUTION REACTION  $\text{Co}(\text{CO})_3\text{NO} + \text{P}(\text{C}_6\text{H}_5)_3$  IN ACETONITRILE AND DIMETHYLSULPHOXIDE

Temp. ( $^{\circ}\text{C}$ )	$10^3 [\text{C}]$ (M)	$10^2 [\text{L}]$ (M)	$10^4 k_I (\text{obs.})$ ( $\text{sec}^{-1}$ )	$10^3 k_{II} (\text{obs.})$ ( $\text{l} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ )
<i>In acetonitrile</i>				
25.0	15.10	1.594		3.08
	12.20	2.146		2.99
	12.60	3.634		2.76
	12.68	5.449		2.95
	13.35	6.560		2.79
	13.05	7.739		2.54
	11.35	8.744		2.87
<i>In dimethylsulphoxide</i>				
30.0	5.52	3.437	4.95	14.4
	2.15	3.437	4.34	12.6
	4.11	3.437	4.99	14.5
	3.68	4.960	6.17	12.4
	4.02	4.960	5.95	12.0
	3.18	4.960	6.29	12.7
	3.43	7.462	8.52	11.4
	3.80	7.462	8.25	11.1
	6.38	7.462	9.06	12.1
	10.20	10.360	12.20	11.8
	3.35	10.360	11.25	10.9
	5.25	10.360	11.07	10.7

<sup>a</sup> See rate eqn. in the text.

TABLE 4

FIRST- AND SECOND-ORDER RATE CONSTANTS  $k_1^a$  AND  $k'^a$  FOR THE MONOSUBSTITUTION REACTIONS  $\text{Co}(\text{CO})_3\text{NO} + \text{As}(\text{C}_6\text{H}_5)_3$  AND  $\text{Co}(\text{CO})_3\text{NO} + \text{P}(\text{C}_6\text{H}_5)_3$  IN DIFFERENT SOLVENTS

Solvent	Temp. (°C)	$\text{As}(\text{C}_6\text{H}_5)_3$		$\text{P}(\text{C}_6\text{H}_5)_3$	
		$10^6 k_1$ ( $\text{sec}^{-1}$ )	$10^5 k'$ ( $\text{l} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ )	$10^6 k_1$ ( $\text{sec}^{-1}$ )	$10^3 k'$ ( $\text{l} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ )
Cyclohexane	40.0	0.5	0.84		
	45.0	1.20	1.40		
	50.0	2.54	2.25		
Benzene <sup>b</sup>	27.1			0.05	1.19
	39.4	1.20	1.40		
	46.4	2.90	2.70	2.90	5.45
	52.3	7.50	4.10	8.40	9.14
Toluene	25.0				1.00 <sup>c</sup>
	40.0	1.05	1.00		
	45.0	2.24	1.66		
Nitromethane	50.0	4.39	2.50		
	25.0				2.60 <sup>c</sup>
	44.7	4.49	5.90		
Tetrahydrofuran	50.0	11.0	8.50		
	25.0				1.30 <sup>c</sup>
	40.0	18.8	1.55		
Acetonitrile	45.0	37.0	1.98		
	60.0	66.0	3.55		
	25.0				2.85
	30.0	13.7			
Dimethylsulphoxide	35.5	25.2			
	40.0	38.1			
	30.0	133.0		132.0	9.79
	35.0	277.0			
	40.0	416.0			

<sup>a</sup> See rate eqn. in the text. <sup>b</sup> From ref. 9. <sup>c</sup> From refs. 17 and 24.

reagents. However, the  $k_1$  values in  $\text{CH}_3\text{CN}$ , THF and DMSO are much higher ( $10^2$  to  $10^3$  times), clearly pointing to different solvent behaviour. This may originate in coordination from the solvent. The coordinating ability can be measured by the donor number  $DN(\text{SbCl}_5)$  shown in table 5, which represents<sup>20,21</sup> the ability of the solvent to give complexes with  $\text{SbCl}_5$  relative to that of 1,2-dichloroethane. As suggested in similar cases<sup>2,3,8</sup>, it can be assumed that for the first-order path a reaction scheme:



occurs, involving some kind of solvent association with the substrate, and it is noteworthy that carbonyl complexes with  $\text{CH}_3\text{CN}$  ligands are known<sup>22</sup>.

The activation parameters shown in Table 5 give further information on the nature of the postulated solvent interaction. The values in the non-donor solvents cyclohexane, toluene and nitromethane agree with those previously<sup>9</sup> measured in benzene, confirming the essentially pure dissociative character of the reaction. In solvents of increasing donor ability ( $\text{CH}_3\text{CN}$ , THF and DMSO) a gradual shift from

TABLE 5

COMPARISON OF RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REACTION  $\text{Co}(\text{CO})_3\text{NO} + \text{As}(\text{C}_6\text{H}_5)_3$  AT  $40.0^\circ$ 

Solvent	Dielectric constants	$DN (\text{SbCl}_5)^a$	$10^6 k_1^b$ ( $\text{sec}^{-1}$ )	$10^5 k'^b$ ( $\text{l} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ )	I order		II order	
					$\Delta E^\ddagger$ ( $\text{kcal} \cdot \text{mole}^{-1}$ )	$\Delta S^\ddagger$ (e.u.)	$\Delta E^\ddagger$ ( $\text{kcal} \cdot \text{mole}^{-1}$ )	$\Delta S^\ddagger$ (e.u.)
Cyclohexane	2.02(20°)		0.5	0.84	30.0	+7	18.7	-24
Benzene <sup>c</sup>	2.28(20°)		1.32	1.48	31.1	+14	17.0	-28
Toluene	2.38(25°)		1.05	1.00	29.4 <sup>d</sup>	+6 <sup>d</sup>	18.6	-24
Nitromethane	35.87(30°)	2.07	2.01 <sup>e</sup>	4.24 <sup>e</sup>	34.0	+22	14.0	-36
Tetrahydrofuran	7.70(25°)	20.0	18.8	1.55	24.7	-4	20.0	-16
Acetonitrile	38.8 (20°)	14.1	38.1		18.0	-23		
Dimethylsulphoxide	48.9 (20°)	29.8	416.0		21.0	-10		

<sup>a</sup> Donor numbers from ref. 20. <sup>b</sup> See rate eqn. in the text. <sup>c</sup> From ref. 9. <sup>d</sup> Thorsteinson and Basolo<sup>17</sup> give  $\Delta H^\ddagger$  30 kcal/mole and  $\Delta S^\ddagger$  (289°K) +10 e.u. <sup>e</sup> Values extrapolated to 40.0° from the present data.

the mean of the above values is observed. At the limit, in  $\text{CH}_3\text{CN}$ , the activation parameters agree with those expected for an associative mechanism.

Such a gradual shift of the activation parameters for the first-order path in the last three solvents, indicates that the solvent lowers the Co-C bond energy in the transition state. The general mechanism may therefore be considered a solvent-assisted dissociative process<sup>2,22</sup> ranging from an almost pure dissociative path in benzene, cyclohexane and toluene, to an essentially associative process in  $\text{CH}_3\text{CN}$ . The behaviour of this last solvent is noteworthy in that it partly deviates from what would be expected on the basis of its donor ability. This effect, which has been observed in other reactions<sup>5</sup>, probably reflects the intervention of other factors, *e.g.*, some kind of specific interaction with the substrate, or a steric effect.

The activation parameters for the second-order path are those expected for a mechanism involving association with the ligand. On increasing the dielectric constant of the non-coordinating solvents values of  $k_1$  and usually those of  $k'$ , increase both for  $\text{As}(\text{C}_6\text{H}_5)_3$  and  $\text{P}(\text{C}_6\text{H}_5)_3$ . The increase of the  $k'$  rate constants, which is larger than that of the  $k_1$ 's, reflects the increased polarity of the pentacoordinated activated complex with respect to the substrate.

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