Vibrational Spectra and Structures of Organolead Compounds. I. Methyllead Halides

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Abstract: The infrared and Raman spectra of the trimethyllead halides, Me_3PbX (X = F, Cl, Br, or I), and dimethyllead dihalides, Me_2PbX_2 (X = Cl or Br), have been recorded over the range 4000–70 cm^{-1} in the solid state and also, where possible, in solution. Molecular weight measurements have also been carried out for two of the trimethyl derivatives. The combined data indicate that, whereas all the halides are monomeric in noncoordinating solvents, in the solid state they are associated by way of halogen bridging. The methyllead halides are more associated than the analogous methyltin halides. Assignments for the various fundamentals are presented and approximate PbX stretching force constants calculated.

Although compounds of the types R_3PbX and R_2PbX_2 (R = alkyl or aryl group, X = an electronegative group, especially halogen) have been known for many years, until recently very little was known about their structures. They are, in general, white crystalline solids, many of which melt with difficulty or decompose on heating. They have only slight solubility in organic solvents, those of the type R_2PbX_2 being less soluble in all solvents than those of the type R_3PbX.

The dipole moments of the trialkyllead halides in solution are high (*e.g.*, Et_3PbBr is 4.88 D),[1] suggesting that the lead–halogen bond is largely ionic. This has led to the suggestion that such compounds are completely ionic, and, in particular, that trialkylplumbonium ions might be planar.[2] On the other hand, as shown in the present paper, the trialkyllead halides are monomeric in benzene solution, so that, at least in this state, covalent PbX bonds are retained.

In the solid state, several lines of evidence suggest that the alkyllead halides are associated. The melting points of the trimethyl compounds,[2,3] which, except for the fluoride, are over 100° above those of the analogous tin compounds (Table I), are particularly suggestive in this regard. They decrease in the order F > Cl > Br > I, this being probably a rough guide to the strength of the association. Both dimethyllead dichloride and dibromide decompose before melting, whereas the corresponding tin compounds have low melting points. Dimethyllead diiodide is unstable[4] and has not yet been prepared pure; dimethyllead difluoride has also not yet been prepared.

Table I. Melting Points of the Group IV Trimethylmetal Halides and Dimethylmetal Dihalides (°C)[a]

Compound	M =			
	Si	Ge	Sn	Pb
Me_3MF	−74		d 375	d 305
Me_3MCl	−58	−13	37	d 190
Me_3MBr	−43	−25	27	133
Me_3MI			3	106
Me_2MF_2	−87		d 360	
Me_2MCl_2	−86	−22	108	d 230
Me_2MBr_2	−58		74	d 200
Me_2MI_2			30	

[a] d = decomposition.

The infrared spectra of the trimethyllead halides in the solid state only have recently been reported[5] down to 400 cm^{-1}. However, it seemed most desirable that both the infrared and the Raman spectra of these halides, as well as of the dimethyllead dihalides, should be recorded accurately over a wider frequency range for solutions as well as for Nujol mulls. In this way, detailed structural information on the compounds for both states could be obtained. Of most value in this regard is a study of the metal–ligand stretching frequency region (approximately 100–500 cm^{-1}). Thus Clark and Williams[6] have shown that SnCl stretching frequencies of alkyltin chlorides are lowered by some 80–100 cm^{-1} on formation of six-coordinate adducts, and similar effects have since been found for the corresponding bromides and iodides.[7] Moreover, the SnCl stretching frequencies of trimethyltin chloride[6,8] and dimethyltin dichloride[6,9] are some 20–30 cm^{-1} lower in the solid state than in solution in nonpolar solvents, indicating weak association in the solid state.

Accordingly, we have laid particular emphasis on the PbC and PbX stretching frequencies in the present study. The structural information gained in this way has been coupled with that from molecular weight measurements and discussed with reference to the known structures of trimethyltin fluoride[10] and dimethyltin difluoride.[11]

Experimental Section

Preparation of Compounds. Tetramethyllead was supplied by the Associated Octel Co. as a 68% w/w solution in toluene and was used as such in the preparation of the methyllead halides.

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Table II. The Infrared and Raman Spectra of the Trimethyllead Halides in the Solid State

	Me_3PbF		Me_3PbCl		Me_3PbBr		Me_3PbI[a]
Assignment	Raman	Ir	Raman	Ir	Raman	Ir	Ir
$\nu_a(CH_3)$	3019 w	3019 s	3024 m	3021 s	3025 w	3023 s	3020 m
$\nu_s(CH_3)$	2928 m	2928 s	2928 s	2927 s	2930 s	2928 s	2925 s
$2x\delta_a(CH_3)$		2780 w		2776 m		2774 m	2770 w
$2x\delta_s(CH_3)$		2291 m		2283 m		2288 m	2281 m
		1622 vw				1641 vw	1632 vw
$2x\rho(CH_3)$				1605 vw		1609 w	1600 w
$\delta_a(CH_3)$		1451 m br					
		1406 s, br	1406 w, br	1398 s, br	1402 vw	1396 s, br	1393 s, br
$\delta_s(CH_3)$	1174 s	1173 m	1174 s				
	1167 m	1168 m		1166 m	1163 s	1167 m	1163 s
	1164 sh	1161 m	1155 s	1149 s	1150 m	1154 s	1149 s
		1148 s		1142 s		1149 s	1146 m
$2x\nu_a(PbC_3)$						982 w, br	
		853 m, sh				854 m	854 m
$\rho(CH_3)$		789 vs, br		784 vs, br		784 vs, br	780 vs, br
		726 m, sh					
		654 w				655 w	656 w
$\nu_a(PbC_3)$	504 s	499 vs	496 s	494 s	494 vs	492 vs	486 vs
				488 vs			
$\nu_s(PbC_3)$	476 vs	468 vw	464 vs	462 vw	464 vs	463 vw	454 w
						158 wm	
$\nu(PbX)$		315 s, br		191 s, br		118 s	105 s
		268 m, br	149 m		121 sh		
Skeletal	161 s	151 s					
modes	123 vs		125 s		127 s		
		112 s		111 m			
				102 s			
				89 s		91 s	91 s

[a] Decomposes immediately in laser beam.

Trimethyllead chloride, trimethyllead bromide, dimethyllead dichloride, and dimethyllead dibromide were prepared by treating tetramethyllead in ethyl acetate solution with the appropriate halogen.[4,12] The trimethyllead halides are formed at −70° and the dimethyllead dihalides at −20°. Trimethyllead chloride was purified by recrystallization from ethyl acetate, and trimethyllead bromide by sublimation. The dimethyllead dihalides were used without further purification. Dimethyllead dibromide was studied immediately after preparation since appreciable decomposition to trimethyllead bromide and lead(II) bromide occurred within a few days.

Trimethyllead iodide, which has been prepared previously[13] but not characterized, was prepared by treating tetramethyllead in ether solution at −70° with iodine. The initial pale-cream solid, mp 104–106°, turned bright yellow over a period of a few weeks owing to its decomposition to lead(II) iodide. Neither dimethyllead difluoride nor dimethyllead diiodide is apparently yet known.

Trimethyllead fluoride was obtained[14] by adding hydrofluoric acid to an aqueous solution of trimethyllead hydroxide until the solution was neutral. The required compound precipitated as white crystals.

Infrared and Raman Spectral Measurements. The infrared spectra in the region 4000–200 cm^{-1} were recorded on a Perkin-Elmer 225 spectrometer. Solids were run as Nujol or hexachlorobutadiene mulls while solution studies were carried out using carbon tetrachloride or benzene as solvents; potassium bromide or cesium iodide plates or cells were used. The spectra in this region were calibrated against those of a number of standard compounds. The low-frequency spectra were recorded on Grubb–Parsons instruments, Types DM 2 (455–200 cm^{-1}) and GM 3 (200–70 cm^{-1}), as Nujol mulls or benzene solutions and using polythene plates or cells. The spectra in this region were calibrated against that of water vapor.[15] Spectra below 200 cm^{-1} were recorded at liquid nitrogen temperatures in order to improve resolution.

The Raman spectra were recorded on a Cary 81 spectrometer fitted with a helium–neon (6328 Å) laser source. Spectra were recorded on the solid powders, packed into the standard metal cone supplied with the instrument or as benzene solutions sealed into glass capillaries. The spectra were calibrated against the emission lines of neon. We are grateful to the University of London for making this instrument available.

Molecular Weight Measurements. The molecular weights of trimethyllead bromide and trimethyllead iodide were determined in benzene solution using a Mechrolab vapor pressure osmometer. Trimethyllead chloride and the dimethyllead dihalides were insufficiently soluble for molecular weight determinations. The results were 330 for Me_3PbBr at 4.6×10^{-2} *M* (calculated for monomer, 332) and 384 for Me_3PbI at 9.2×10^{-2} *M* (calculated for monomer, 379).

Results and Discussion

The infrared and Raman spectra of the trimethyllead halides are in Tables II and III, while those for the dimethyllead dihalides are in Table IV. It is most convenient to discuss the spectra of the trimethyllead halides first, and in terms of (a) methyl group vibrations, (b) PbC stretching vibrations, (c) PbX stretching vibrations, and (d) skeletal bending vibrations. The interpretation follows closely that of methyltin halides[16] and of tetramethyllead.[17,18]

A. Trimethyllead Halides. (a) **Methyl Group Vibrations.** The trimethyllead halides have been shown to be monomers in benzene solution, and they should therefore have C_{3v} symmetry assuming either free rotation about the C–Pb bonds or locking of the hydrogen atoms into either of their most symmetric arrangements (Figure 1).

With the hydrogen atoms in either of the locked-in positions, the CH stretching vibrations reduce to $2a_1 + a_2 + 3e$; apart from the a_2 mode, which is inactive, the remaining five modes should be both infrared and

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Table III. The Infrared and Raman Spectra of the Trimethyllead Halides in Solution[a]

Assignment	Me_3PbCl Raman	Me_3PbCl Ir	Me_3PbBr Raman	Me_3PbBr Ir	Me_3PbI Raman	Me_3PbI Ir
$\nu_a(CH_3)$	*b*	*b*	*b*	3020 m	*b*	3017 m
$\nu_s(CH_3)$				2929 s		2929 s
$2x\delta_a(CH_3)$				2775 w		2773 w
$2x\delta_s(CH_3)$				2300 m		2298 m
				1643 w		1637 w
				1613 w?		1610 w?
$\delta_a(CH_3)$				1396 m, br		1397 m, br
$\delta_s(CH_3)$			1174 s	1172 m	1171 s	1172 s
			1160 m	1158 s	1158 m	1157 s
$\rho(CH_3)$				788 vs, br		782 vs, br
$\nu_a(PbC_3)$	491 s	489 vs	489 s	487 vs	487 s	481 vs
$\nu_s(PbC_3)$	464 vs, p	461 m	462 vs, p	459 m	460 vs, p	455 m
$\nu(PbX)$	279 s	281 vs	186 s, p	186 vs	147 s, p	145 s
$\delta(CPbC)$						128 m, br

[a] Solutions are in carbon tetrachloride (above 900 cm^{-1}), bromoform (900–600 cm^{-1}), and benzene (below 600 cm^{-1}). Trimethyllead fluoride is insoluble. [b] Insufficiently soluble in CCl_4 to observe spectrum.

Table IV. The Infrared and Raman Spectra of the Dimethyllead Dihalides in the Solid State

Assignment	Me_2PbCl_2 Raman	Me_2PbCl_2 Ir	Me_2PbBr_2 Raman	Me_2PbBr_2 Ir
$\nu_a(CH_3)$	3049 w	3041 m	3036 w	3020 m
$\nu_s(CH_3)$	2938 s	2936 s	2929 s	2920 s
$2x\delta_s(CH_3)$		2333 m		
		1644 vw		
		1626 vw		
$\delta_a(CH_3)$		1394 s, br		1414 m, br
				1397 s, br
$\delta_s(CH_3)$	1196 s		1187 s	
	1180 vw	1184 s	1160 w	1160 s
			1150 w	1154 sh
$\rho(CH_3)$		837 vs, br		821 s, br
				602 w
$\nu_a(PbC_2)$		534 w		523 w
$\nu_s(PbC_2)$	460 vvs		447 vs	
$\nu(PbX)$	202 m	202 s, vbr		178 sh
				166 s
	178 s		147 m	
	159 vs		136 s	
				128 s, br
$\delta(CPbC)$?	117 m	114 s, vbr		87 s, vbr

Raman active. However, both in solution and in the solid state, only two bands attributable to CH stretching vibrations can be observed in either the infrared or the Raman spectra. Thus the hydrogen atoms of the three methyl groups attached to the lead atoms must be essentially uncoupled from each other, behaving simply as a single methyl group attached to a heavy point mass. A similar observation has been made for the methyltin halides.[16] There are only slight (≤ 20 cm^{-1}) differences between the frequencies of the CH stretching vibrations in the solid state and in solution, and no structural information can be derived from their study. By analogy with the spectra of related molecules,[18] the lower frequency band (at ~2920 cm^{-1}) is assigned to the symmetric (a_1) CH stretching vibration, whereas the higher frequency one is assigned to the asymmetric (e) vibration.

The CH_3 asymmetric deformation vibrations at ~1390 cm^{-1} and the CH_3 rocking mode at ~780 cm^{-1} both occur as strong broad bands in the infrared but are either very weak or unobserved in the Raman spectra. The other fundamentals and certain overtones are included and assigned in the tables and do not call for special comment.

(b) Pb–C Stretching Vibrations. In the dissolved state, the trimethyllead halides have two PbC stretching vibrations, both active in the infrared and in the Raman, as expected for molecules of C_{3v} symmetry. The lower frequency band, at ~460 cm^{-1}, occurs as a medium band in the infrared and as a strong, polarized band in the Raman, and is thus assigned unambiguously as the $a_1(\nu_s)$ symmetric stretch. The higher frequency band, at ~490 cm^{-1}, occurs as a strong to very strong band in the infrared spectra, but weaker in the Raman spectra, and is assigned to the $e(\nu_a)$ asymmetric stretch.

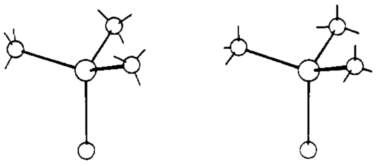


Figure 1. Alternative locked-in structures for trimethyllead halides in solution.

The symmetric (a_1) and asymmetric (t_2) Pb–C stretching vibrations of liquid tetramethyllead at 10° occur, from the Raman spectrum, at 462 and 475 cm^{-1}, respectively;[18] thus the degeneracy-weighted average Pb–C stretching frequency is 472 cm^{-1}. Likewise, the degeneracy-weighted average Pb–C stretching frequencies of the trimethyllead halides are, also from their Raman spectra, 482, 480, and 478 cm^{-1} for chloride, bromide, and iodide, respectively. The order of these mean frequencies, that is, $Me_3PbCl > Me_3PbBr > Me_3PbI > Me_4Pb$, is the same as that found for the analogous tin compounds,[6,7] except that the differences between the mean frequencies are slightly less pronounced for the methyllead halides. As previously argued for the alkyltin halides,[6,7] these mean metal–carbon stretching frequencies are considered to be determined by the effective nuclear charge on the central metal atom, being highest for those compounds which contain the most electronegative halogen atom.

In the solid state, the Pb–C stretching frequencies are within 10 cm^{-1} of their values in solution. However, in the solid state, the symmetric Pb–C stretching frequency is very much weaker relative to the asymmetric one than is the case in solution, suggesting that the PbC_3 skeleton is virtually planar in the solid state.

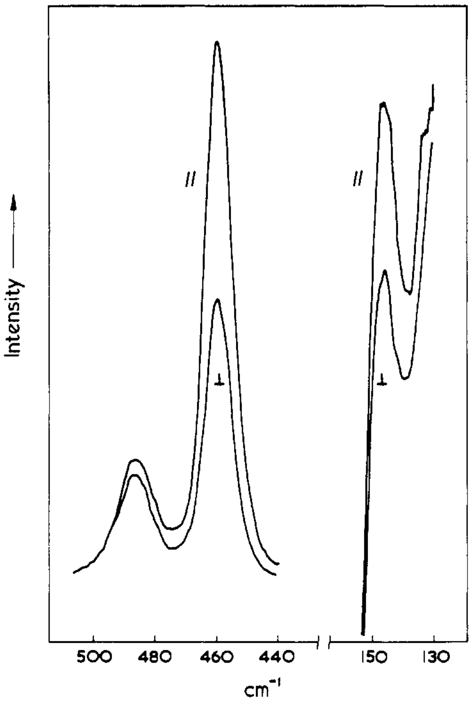


Figure 2. Raman spectrum of $(CH_3)_3PbI$ in benzene solution, including polarization data.

We recognize that this is only one suggestion which is consistent with the facts; it is weakened by the knowledge that for some molecules there are marked alterations in the intensities of given infrared bands on change of state without any accompanying structural change.

(c) Pb–X Stretching Vibrations. In solution in benzene, the lead–halogen stretching frequencies of the trimethyllead halides occur at 279, 186, and 147 cm^{-1} for the chloride, bromide, and iodide, respectively. Assuming a diatomic model for these molecules, in which the effective mass of the lead atom is taken to be $207.2 + 3 \times 15.0 = 252.2$, the PbX force constants are calculated to be 1.41, 1.24, and 1.07 mdyn/Å for X = Cl, Br, and I, respectively.

The Raman bands associated with the Pb–Br and Pb–I stretching vibrations are strongly polarized, confirming that the vibration is totally symmetric (Figure 2); the chloride was insufficiently soluble for polarization studies to be carried out. Trimethyllead fluoride was not found to be soluble in any solvent.

The appearance of bands in the solid-state spectra of those compounds attributable to Pb–X stretching vibrations immediately dispels the suggestion[2] that they may be completely ionic. The most revealing structural information on these compounds derives from a comparison of the Pb–X stretching frequencies for the dissolved and solid states. In the latter, the infrared-active Pb–X stretching frequencies are at 315, 191, 118, and 105 cm^{-1} for X = F, Cl, Br, or I, respectively; these are 88–40 cm^{-1} below the corresponding solution values, and, by analogy with other systems,[19] they strongly suggest that the lead atoms have higher coordination numbers in the solid state than in solution. Moreover, the infrared-active Pb–X stretching frequencies are not, in general, Raman active, and the Raman-active ones are not infrared active.

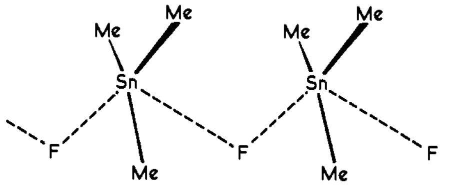


Figure 3. Structure of solid trimethyltin fluoride.

Both lines of evidence, in agreement with the conclusions from the section on Pb–C stretching vibrations, suggest that the local symmetry of the lead atom is close to D_{3h}. However, the fact that the symmetric Pb–C stretch occurs in the infrared at all, as well as the splitting of the asymmetric PbC band in the infrared spectrum of the chloride, suggests that the local symmetry of the lead atom is actually lower than D_{3h}; the most probable structure for these halides in the solid state, consistent with the above facts, is that found by means of X-ray diffraction for trimethyltin fluoride,[10] *i.e.*, as shown in Figure 3.

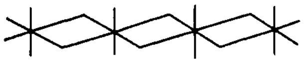
(d) Skeletal Bending Modes. The skeletal bending frequencies of tetramethyllead occur[18] at 130 cm^{-1} (t_2 mode) and 145 cm^{-1} (e mode). In the solution spectrum of trimethyllead iodide there is a band at 128 cm^{-1} which is thus assigned as the CMC skeletal deformation. However, the chloride and bromide were insufficiently soluble to observe these bands in solution in the infrared, and all three were insufficiently soluble for solution Raman spectral measurements around 100 cm^{-1}.

In the solid state, apart from a band at 151 cm^{-1} in the infrared spectrum of the fluoride (probably attributable to a Pb–F–Pb bending vibration), the compounds all contain bands in the 89–123-cm^{-1} region of their infrared and Raman spectra, which are likely to arise from C–Pb–C bending vibrations. They yield, however, no structural information because of their breadth.

B. Dimethyllead Dihalides. Dimethyllead dichloride and dimethyllead dibromide are insufficiently soluble in any convenient solvent for solution infrared or Raman spectral studies, and hence the following discussion is limited only to their structures in the solid state.

(a) Methyl Group Vibrations. The two methyl groups attached to each lead atom in these compounds are not noticeably coupled to one another because only two bands attributable to CH stretching vibrations are observed in their infrared or Raman spectra. The situation is evidently analogous to that already discussed above for the trimethyllead halides. The other methyl group vibrations are assigned in Table IV.

(b) Pb–C Stretching Vibrations. There are two likely polymeric structures for dimethyllead dichloride and dimethyllead dibromide in the solid state. One is that found for diphenyllead dichloride,[20] which is characterized by Cl_2PbCl_2 coplanar chains, with the Pb–C bonds nearly perpendicular to the plane of the chain, *viz.*



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The other is that found for dimethyltin difluoride;[11] it is similar to that above, except that the tin and fluorine atoms form an infinite sheet with the formula $(SnF_2)_\infty$, the Sn–C bonds being perpendicular to the infinite sheet. The local symmetry of the metal atom is D_{2h} in the former but D_{4h} in the latter. The former structure is the more likely for the dimethyllead dihalides, because the latter involves linear or nearly linear metal–halogen–metal bonds, and these are rarely found other than for fluoro complexes.

On the basis of D_{2h} selection rules, the Pb–C stretching frequencies are of the following types: a_g (Raman active only) and b_{1u} (infrared active only). The spectra of the compounds are consistent with these predictions: the lower frequency band in each case (at 460 and 447 cm^{-1} for chloride and bromide, respectively) occurs as a very strong band in the Raman spectra only and is accordingly assigned as the symmetric Pb–C stretch; the higher frequency band in each case (at 534 and 523 cm^{-1} for chloride and bromide, respectively) occurs as a weak band in the infrared spectra only and is assigned as the asymmetric Pb–C stretch.

(c) Pb–X Stretching Frequencies. The halogen-bridged polymeric nature of the dimethyllead halides in the solid state is most clearly demonstrated by the low values for the Pb–X stretching frequencies. These occur in the range 159–202 cm^{-1} for the chloride, when values of about 300 cm^{-1} would be expected for the monomeric species, by analogy with the spectra of trimethyllead chloride and dimethyltin dichloride in solution.[6,8,9]

On the basis of D_{2h} selection rules, the PbX stretching frequencies are of the following types: a_g and b_{1g} (Raman active only) and b_{2u} and b_{3u} (infrared active only). These selection rules are seen (Table IV) in general to hold well in the spectra of the compounds and provide some support for the suggested structure for the molecules. However, the bands are very broad, especially in the infrared, presumably as a result of solid-state splittings.

(d) Skeletal Bending Frequencies. The C–Pb–C bending frequencies occur near 100 cm^{-1}, but are not sufficiently detailed to warrant separate discussion.

Conclusion

Molecular weight measurements on the trimethyllead halides in benzene solution have shown that these compounds are monomers; vibrational spectral work is fully consistent with this conclusion. In the solid state, however, the spectral work in general, and especially that in the Pb–X stretching region, suggests that the compounds have halogen-bridged polymeric structures. The high melting points and low solubilities of the compounds also point to their polymeric nature. The lead atoms are probably five-coordinate with nearly planar PbC_3 groupings.

The dimethyllead dihalides were insufficiently soluble for solution studies, but in the solid state they are clearly polymeric on the bases of high melting points, low solubilities, and low Pb–X stretching frequencies. They are likely to be chain polymers with the diphenyllead dichloride structure.

The lead compounds have a greater tendency to polymerize than have the analogous tin compounds; this is consistent with the larger lead atoms greater preference for a higher coordination number.

The Kinetics and Mechanism of Nucleophilic Substitution in Nickel Tetracarbonyl

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Abstract: The rate of the substitution reaction (1) of nickel carbonyl with triphenylphosphine or carbon monoxide has been measured over a 30° temperature range, in solution in *n*-hexane and toluene (Ph_3P only), and in the gas phase (CO only). The reactions were followed by infrared spectrophotometry in the C–O stretching region, using $C^{18}O$ for the CO exchange reactions. The rates are independent of concentration or type of nucleophile, but first order with respect to $Ni(CO)_4$ concentration. Rates of reaction in the gas phase or in toluene are *ca.* twice those in *n*-hexane, but activation parameters for all reactions are similar (ΔH^* from 22 to 24 kcal mol^{-1}, ΔS^* from +7 to +14 eu). In particular, and contrary to earlier results, CO and Ph_3P in the same solvent react with indistinguishable rates and activation parameters and compete for the same activated complex. Taken in conjunction with the results for the thermal decomposition of $Ni(CO)_4$, in the following paper, the dissociative (S_N1) mechanism (eq 9 and 10) is suggested for the reaction.

The object of the experiments reported here is to establish a plausible mechanism for the substitution reactions of nickel carbonyl (1), where L = CO, R_3P,

$$Ni(CO)_4 + L = Ni(CO)_3L + CO \quad (1)$$

$(RO)_3P$, RNC, and nucleophiles of similar type.

The position[1,2] until recently was that CO reacted by a mechanism different from other nucleophiles, the latter reacting by a common mechanism. Kinetic studies of ^{14}CO exchange (by radioactivity counting[3–5])

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