Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

SOLVENT EFFECTS ON THE IODINE CLEAVAGE OF TETRAORGANOLEAD COMPOUNDS

GIUSEPPE PILLONI* AND GIUSEPPE TAGLIAVINI
Istituto di Chimica Analitica, Università di Padova (Italia)

(Received June 12th, 1967; in revised form September 15th, 1967)

INTRODUCTION

Electrophilic substitution at a saturated carbon centre using tetraorganolead substrates has been recently examined by several authors[1-5]. Our previous results[5] on the reactivity of R_4Pb compounds (R = Me, Et and Pr) with iodine in alcoholic solvents and acetonitrile indicated that solvation at the transition state could be a very important factor in determining the reactivity in such polar media.

The nature of the solvent seems to be of importance generally in organometal substitutions: the assistance of anionic species in the acetolysis of tributyltin hydride has been noted by Dessy *et al.*[6], who worked in DMSO or DMSO/diglyme solvents, but such an effect is not found in methanol[7]. In organometallic substitutions there are several examples[8] in which the metal centre may be subject to nucleophilic assistance, and this is sometimes of importance in establishing the course of the electrophilic attack.

The present paper deals with the examination of the effects produced by nucleophilic solvents on the mechanistic pathway S_F2 found for the reaction between iodine and tetraorganoleads in carbon tetrachloride. The possible assistance by I^- or I_3^- species in acetone and acetonitrile is also discussed.

EXPERIMENTAL

Chemicals, reagents and procedure

Tetraorganoleads were prepared and purified as previously described[5]. All the solvents used were purified as described in the literature[9]. Anhydrous salts and resublimated iodine were used.

Reactions of R_4Pb compounds with iodine were followed spectrophotometrically[10] under pseudo first-order conditions (excess of R_4Pb). The absorbance (of I_2 at λ_{max} 513 mμ in CCl_4, 297 mμ in benzene and of I_3^- at λ_{max} 360 mμ in acetone) against time was recorded by means of a UNICAM SP 800 Spectrophotometer (Cambridge, England) supplied with SP 820 Control Unit and SP 825 Programme Controller accessories suitable for kinetic work. Values of k_{obs} ($l \cdot mole^{-1} \cdot sec^{-1}$) are subject to ±1.5% experimental error.

---

* Ricercatore Incaricato C.N.R.

RESULTS

The second order rate constants k_2(l·mole^{-1}·sec^{-1}) for the reaction of iodine with the tetraorganolead compounds in carbon tetrachloride and benzene are listed in Table 1. The results concerning the reactions carried out in acetone are summarized in Table 2.

TABLE 1

IODINE CLEAVAGE OF TETRAALKYLLEADS IN CARBON TETRACHLORIDE AT 31° AND BENZENE AT 35°
Kinetic constants k_2 in l·mole^{-1}·sec^{-1}.

Compound	k_2	
	CCl_4	C_6H_6
Me_4Pb	0.0355	1.9
Et_4Pb	1.08	22.8
Pr_4Pb	0.43	7.1

TABLE 2

IODINE CLEAVAGE OF TETRAALKYLLEADS IN ACETONE AT 35°
$[NaI]+[NaClO_4]=0.1$, $[I_3^-]=5\times10^{-5}$; kinetic constants k_{obs} and k_2 in l·mole^{-1}·sec^{-1}.

NaI concn. $\times 10^3$ (mole/l.)	k_{obs}	$k_{obs}\cdot[NaI]$ $\times 10^3$	$k_{obs}\cdot[I^-]$ $\times 10^3$	$k_2=k_{obs}\cdot[I^-]\cdot K^a$
Tetramethyllead				
2	0.28	0.560	0.443	(443)
3	0.20	0.600	0.439	(439)
4	0.16	0.640	0.439	(439)
5	0.13	0.650	0.422	(422)
Tetraethyllead				
2	0.105	0.210	0.166	(166)
3	0.074	0.222	0.163	(163)
4	0.060	0.240	0.164	(164)
5	0.050	0.250	0.162	(162)

[a] On assuming $K = 10^6$.

In this solvent it is necessary to work in the presence of excess of iodine ions, as acetone reacts with iodine. Under such conditions the observed rate law $v=k_{obs}\cdot[R_4Pb]\cdot[I_3^-]$ may involve the three simultaneous mechanisms[4]:

$$v_1=k_1\cdot[R_4Pb]\cdot[I_3^-],\quad v_2=k_2\cdot[R_4Pb]\cdot[I_2] \text{ and } v_3=k_3\cdot[R_4Pb]\cdot[I^-]\cdot[I_2],$$

from which the following equation results:

$$k_{obs}\cdot[I^-]=k_2/K+(k_1+k_3/K)\cdot[I^-] \tag{1}$$

where K represents the stability constant of the equilibrium $I^-+I_2\rightleftharpoons I_3^-$ in acetone.

From Table 2 it appears that the product $k_{obs}\cdot[NaI]$ is not constant for varying NaI concentration. On the other hand if partial dissociation of NaI in acetone is taken into account by use of the value $K_c = 6 \times 10^{-3}$ at 35°, as deduced from reported values[11-12], the $k_{obs} \cdot [I^-]$ product appears to be fairly constant.

In addition the k_2 values have been calculated by assuming that the value of K in acetone is not greater than 5×10^5 to 1×10^6 at 35°, as indicated by our measurements. Table 3 lists the k_2 values for acetone together with those obtained in a previous work[5] on various alcohols and acetonitrile.

TABLE 3

IODINE CLEAVAGE OF TETRAALKYLLEADS IN POLAR SOLVENTS
Kinetic constants k_2 in $l \cdot mole^{-1} \cdot sec^{-1}$.

Compound	Acetone (35°)	n-Propanol (25°)	Ethanol (25°)	Methanol (25°)	Acetonitrile (25°)
Me_4Pb	(436)	1,610	2,800	9,410	241,000
Et_4Pb	(164)	730	1,330	3,660	93,000
Pr_4Pb		100	200	1,260	20,000

TABLE 4

EFFECT ON RATE BY ADDING POLAR SOLVENTS TO CCl_4
$Me_4Pb + I_2$, at 31°; $[Me_4Pb] = 2 \times 10^{-2}$, $[I_2] = 1 \times 10^{-3}$; concn. in $mole \cdot l \times 10^2$; k^{Sv}_{obs} in $l \cdot mole^{-1} \cdot sec^{-1}$

Added solvent (Sv) to CCl_4

Methanol		Ethanol		n-Propanol		Acetonitrile	
Concn.	k^{Sv}_{obs}	Concn.	k^{Sv}_{obs}	Concn.	k^{Sv}_{obs}	Concn.	k^{Sv}_{obs}
1.66	0.054	2.27	0.070	1.75	0.054	2.54	0.33
3.33	0.11	3.40	0.12	2.63	0.076	3.81	0.70
5.00	0.20	4.53	0.18	3.50	0.11	5.08	1.20
6.00	0.28	5.67	0.26	4.38	0.15	6.35	1.74
6.67	0.34	6.80	0.36	5.25	0.20	7.61	2.60

The effect of the addition of polar solvents to CCl_4 on the reaction rate for tetramethyllead has been examined at 31° (cf. Table 4). The value of k^{Sv}_{obs} is linearly related to the square concentration of the added solvent as shown in Fig. 1. The least squares method gives intercept values for $[Sv] = 0$ of 0.0335; 0.0361; 0.0356 and 0.0554 for Sv = methanol, ethanol, propanol and acetonitrile respectively. The k_2 value for CCl_4 (*cf.* Table 1) at the same temperature is 0.0355 which agrees with the above values.

DISCUSSION

Our previous paper[5] pointed out, in agreement with early reports of Belgian authors on lead[2] and tin alkyls[10-13], that iodine cleavage of tetraorganoleads proceeds via two different mechanisms, namely S_F2 and S_E2, in non-polar and polar solvents respectively. Nevertheless, whereas in non-polar solvents an S_F2 mechanism is quite acceptable, in polar solvents an interpretation of the mechanism in terms of an S_E2 reaction may be arbitrary in view of the fact that nucleophilic assistance in the reaction may occur.

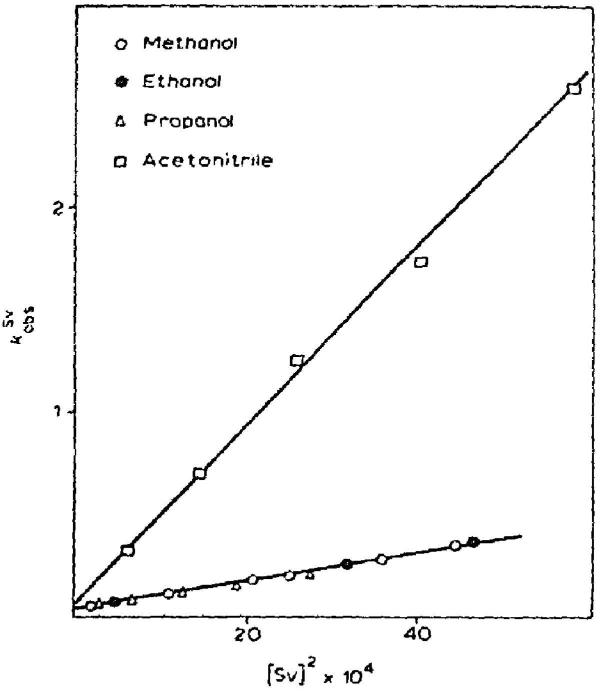

Fig. 1. Effect on k_{obs} for the reaction of iodine with Me_4Pb in CCl_4 by adding known amounts of polar solvents.

From the results for the two non-polar solvents used, it appears that the values of k_2 are greater in benzene than in CCl_4. This might arise from polarization of iodine molecules in benzene as a result of formation of the species $I_2 \cdot C_6H_6$ [14-15].

From the results in polar solvents, particularly those referring to tetramethyllead in acetonitrile (*cf.* Table 5) and those for methyl and ethyl substrates in acetone (*cf.* Table 2) it appears that the product $k_{obs} \cdot [I^-]$ is fairly constant within the limit of experimental error. This shows that the term $(k_1 + k_3/K) \cdot [I^-]$ of eqn. (1) contributes to the total rate to a smaller extent than k_2/K and consequently we can conclude that the species I^- and I_3^- can not play an important role in such solvents. This conclusion does not agree with that recently reached by other authors[4], who stated that I^- species in acetone as well as in acetonitrile can be important in providing nucleophilic assistance in such media. Furthermore it does not agree with the statement

TABLE 5

EFFECT ON RATE FOR TETRAMETHYLLEAD IN ACETONITRILE AT 25° BY VARYING THE I^- CONCENTRATION[a]
$[NaI] + [NaClO_4] = 0.194$

$[NaI] = [I^-]$	k_{obs} ($l \cdot mole^{-1} \cdot sec^{-1}$)	$k_{obs} \cdot [I^-]$
0.029	0.47	0.0136
0.043	0.33	0.0141
0.097	0.15	0.0145

[a] *Cf.* ref. 5.

that I_3^- species in acetonitrile may either (*a*) provide "nucleophilic assistance" (*b*) carry out attack on carbon, or (*c*) facilitate reaction through a four-centre mechanism. In particular, their conclusion that I^- species in acetone assists the reaction seems to be incorrect, because if the partial dissociation of NaI is taken into consideration, eqn. (1) reduces to

$$k_{obs} \cdot [I^-] = k_2/K$$

The results in alcohols (*cf.* Table 3 and ref. 5) further confirm that both I^- and I_3^- species do not participate to the reaction in these media.

From other reports[2] and from our results (*cf.* Table 4) it seems that the reactions can be assisted by participation of solvent in a pre-determining step. This is consistent with the observed decrease in the reactivity with increasing length of the alkyl groups (*cf.* Table 3). This can be interpreted by assuming that the assisting solvent coordinates to a lead centre, the acceptor properties of which are related to the R alkyl groups bonded to it. The $+I$ inductive effect of the R groups increases with increasing chain-length in R, and so coordination of the solvent to the lead centre becomes less important as the chain-length increases, because of inductive as well as steric effects. These conclusions are in agreement with the results obtained[10] in the iodine cleavage of unsymmetrical organotin compounds of the type R_3SnMe, for which the rates in methanol decrease in the order R = Et, Pr, Bu and iso-Pr, although the only leaving group R_3Sn- is responsible for steric or inductive effects and the polarity of the bond R_3Sn-Me increases with increasing R.

The above mentioned conclusions on the influence of the solvents on the mechanism of electrophilic substitution are consistent with the increase in the rate of reaction in CCl_4 when amounts of polar solvents are added to it (*cf.* Table 4). We must note that the greater effect of acetonitrile on k_{obs}^{Sv} compared with the effects of the three alcohols, cannot depend on a different polarization of the iodine molecules by the solvents. In fact, if the wave lengths of maximum absorbance[5] for the complex $I_2 \cdot Sv$ in CCl_4 (Sv = ROH, MeCN : λ_{max} 440 and 456 mμ respectively) are taken as a measure of this polarization[15], it appears that iodine is more polarized in alcohols than in acetonitrile. The different effects of various solvents can be interpreted as being due mainly to the importance of the solvent molecules around the metal centre.

With regard to the linear relationship between the k_{obs}^{Sv} and the square concentration of the employed solvents in our opinion the data are not sufficient to supply a satisfactory explanation: in order to provide evidence for an incipient pentacoordinated trialkyllead ion $R_3PbSv_2^+$ it would be of interest to gain additional knowledge by using non-kinetic techniques.

ACKNOWLEDGEMENT

The financial support of the Consiglio Nazionale delle Ricerche (Roma) is gratefully acknowledged.

SUMMARY

The reaction of iodine with tetraorganolead compounds, R_4Pb (= Me, Et and Pr) has been examined in several solvents.

The effect on the rate of the addition of polar solvents to carbon tetrachloride has been studied in the case of tetramethyllead.

The existence of nucleophilic assistance by coordination of polar solvent to the lead centre is proposed. Assistance by I^- or I_3^- species in acetone and acetonitrile has not been found.

REFERENCES

1 G. C. Robinson, *J. Org. Chem.*, 28 (1963) 843.
2 M. Gielen, J. Nasielski, J. E. Dubois and P. Fresnet, *Bull. Soc. Chim. Belges*, 73 (1964) 293.
3 P. Baekelmans, M. Gielen and J. Nasielski, *Ind. Chim. Belge*, 12 (1964) 1265.
4 M. Gielen and J. Nasielski, *J. Organometal. Chem.*, 7 (1967) 273.
5 L. Riccoboni, G. Pilloni, G. Plazzogna and G. Tagliavini, *J. Electroanal. Chem.*, 11 (1966) 340.
6 R. E. Dessy, T. Hieber and F. Paulik, *J. Amer. Chem. Soc.*, 86 (1964) 28.
7 H. G. Kuivila and P. L. Levins, *J. Amer. Chem. Soc.*, 86 (1964) 23.
8 R. E. Dessy and W. Kitching, *Advan. Organometal. Chem.*, 4 (1966) 268.
9 A. Weissberger (Ed.), *Organic Solvents. Physical Properties and Methods of Purification*, Vol. II, Interscience, New York/London, 1955.
10 M. Gielen and J. Nasielski, *Bull. Soc. Chim. Belges*, 71 (1962) 32.
11 G. Charlot and B. Tremillon, *Les réactions chimiques dans les solvents et les sels fondus*, Gauthier-Villars, Paris, 1963, p. 387.
12 C. A. Kraus and W. C. Bray, *J. Amer. Chem. Soc.*, 35 (1913) 1315.
13 M. Gielen and J. Nasielski, *J. Organometal. Chem.*, 1 (1963) 173.
14 H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 71 (1949) 2703.
15 J. Kleinberg and A. W. Davidson, *Chem. Rev.*, 42 (1948) 601.
16 S. Faleschini and G. Tagliavini, *Gazz. Chim. Ital.*, 97 (1967) 1401.