

## PRELIMINARY COMMUNICATION

### FREE-RADICAL FORMATION FROM ORGANOMETALLIC COMPOUNDS AND HALIDES

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Extensive investigations in recent years have shown that interaction between organic halides and many types of organometallic derivatives in which the metal atom is in a low oxidation state produces free radicals which are capable of initiating the polymerization of vinyl monomers<sup>1</sup>. The concentrations of the organometallic derivative and halide in initiating systems are generally in the ranges  $10^{-3}-10^{-4}$ ,  $10^{-1}-10^{-2}$  mole $\cdot$ l<sup>-1</sup>, respectively, and the temperature lies between 0° and 100°. Under these conditions, kinetic observations show that the organometallic compound does not react directly with the halide, but requires preliminary activation, either by reaction with monomer or solvent, or scission of a ligand from the molecule. For example, with molybdenum carbonyl the first reaction is the reversible S<sub>N</sub>2 process<sup>2</sup>:



in which M represents the vinyl monomer (e.g. methyl methacrylate). A polar solvent with electron-donating properties such as ethyl acetate or *N,N*-dimethylformamide can often take the place of the monomer in this reaction<sup>2,3</sup>. Complex (I) reacts with the halide ClX to form (II):



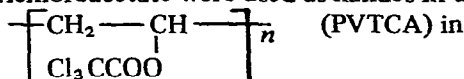
which subsequently yields a radical on decomposition. Radical formation is effectively the result of an electron transfer from (I) to the halide which, in principle, may occur by either of the two routes:



In this communication we show that, in fact, both reactions (3a) and (3b) can occur. As would be expected, (3b) is encouraged by a high electron-affinity of X, but the relative importance of the two reactions depend also on the natures of the metal derivative, the ligands, and possibly the solvent.

Two techniques for distinguishing between (3a) and (3b) have been employed; both make use of polymerization initiated by the free-radical species formed in these reactions.★ In the first technique, a labelled atom ( $^{14}\text{C}$ ) is built into the group X; only (3a) leads to the incorporation of X in the final polymers, so that the contribution of (3a) to the total initiation may be deduced from measurements of the radioactivities of the polymers. The second method utilises the fact that if X is part of a preformed polymer chain (3a) leads to the growth of a branch on this chain, while (3b) does not, since the new polymer molecule growing from the chlorine atom is not attached to the original polymer. If the growing chains terminate by combination of radicals (3a) leads to the formation of a cross-link between two chains of the preformed polymer, and ultimately, when a critical amount of cross-linking has occurred, to gelation. Reaction (3b) cannot give rise to cross-linking or gelation, hence measurement of the gel-time may be used to assess the relative importance of (3a) and (3b). (Corrections are necessary to allow for the effects of chain transfer and the progressive consumption of the reactants on the gel-time, but these will not be discussed here).

Carbon tetrachloride and ethyl trichloroacetate were used as halides in the first method, and polyvinyl trichloroacetate



the second; the repeat unit in this polymer is the analogue of ethyl trichloroacetate and would be expected to show similar reactivity. The organometallic derivatives studied were  $\text{Mo}(\text{CO})_6$ ,  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Pt}(\text{PPh}_3)_4$ ,  $\text{Ni}(\text{CO})_4$ ,  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ ,  $\text{Ni}[\text{P}(\text{OPh})_3]_4$ . Methyl methacrylate was the monomer in all experiments, and the reactions were performed in inactive (sodium) light; with  $\text{Mn}_2(\text{CO})_{10}$ , photochemical initiation with  $\lambda = 4358\text{\AA}$  was employed<sup>4</sup>.

It was found that effectively the whole reaction proceeds according to (3a) with carbon tetrachloride, irrespective of the nature of the organometallic derivative. The temperatures in these experiments were as shown in Table 1. The results with the trichloroacetate esters are summarised in Table 1. While (3a) constitutes practically the whole reaction with the Mo, Mn, and Pt compounds, (3b) is of comparable importance with the Ni derivatives. Both techniques are seen to lead to substantially similar results. Some information about the nature of the radical product of (3b) was obtained with the aid of ethyl trichloroacetates labelled in three different positions. It will be seen from Table 1 that (with  $\text{Ni}[\text{P}(\text{OPh})_3]_4$ ) there is no significant difference between the three halides with regard to the extent to which labelled atoms are incorporated in the polymer; this would be expected if the radical were a chlorine atom (or some species derived from it), but would be difficult to explain otherwise. The possibility that the radical first formed is an adduct of  $\dot{\text{C}}\text{I}$  with a monomer molecule (*i.e.*  $\text{Cl}-\underset{\text{I}}{\overset{\text{I}}{\text{C}}}-\dot{\text{C}}$ ) cannot be excluded on the basis of these results.

★These will be discussed more fully in the paper of C.H. Bamford, G.C. Eastmond and D. Whittle, (in course of publication).

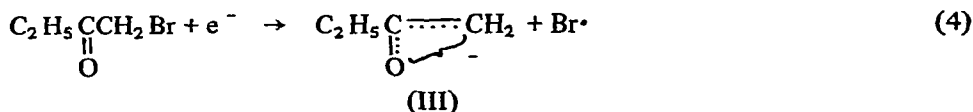
TABLE 1

## REACTIONS OF ORGANOMETALLIC COMPOUNDS WITH TRICHLOROACETATES

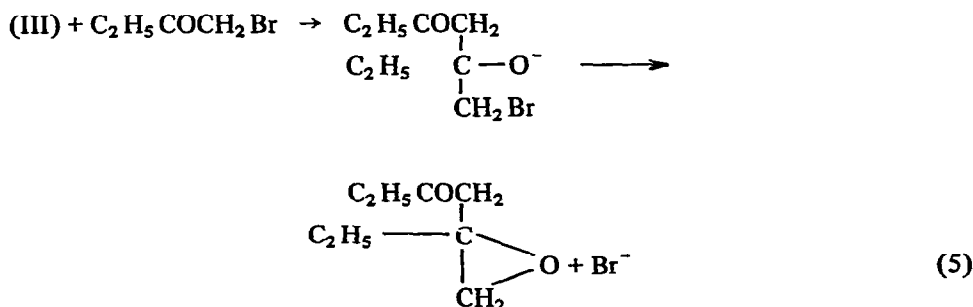
Organometallic compound	Halide	Temperature (°C)	tracer <sup>a</sup> technique	gelation <sup>a</sup> technique
Mo(CO) <sub>6</sub>	CCl <sub>3</sub> <sup>14</sup> COOEt	80	100	—
	PVTCA	80	—	100
Mn <sub>2</sub> (CO) <sub>10</sub>	CCl <sub>3</sub> <sup>14</sup> COOEt	25	100	—
	PVTCA	25	—	100
Pt(PPh <sub>3</sub> ) <sub>4</sub>	CCl <sub>3</sub> <sup>14</sup> COOEt	60	100	—
	PVTCA	60	—	100
Ni(CO) <sub>4</sub>	CCl <sub>3</sub> <sup>14</sup> COOEt	25	60	—
	PVTCA	25	—	64
Ni(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	CCl <sub>3</sub> <sup>14</sup> COOEt	25	77	—
	PVTCA	25	—	81
Ni[P(OPh) <sub>3</sub> ] <sub>4</sub>	CCl <sub>3</sub> <sup>14</sup> COOEt	25	53	—
	<sup>14</sup> CCl <sub>3</sub> COOEt	25	59	—
	CCl <sub>3</sub> COO <sup>14</sup> CH <sub>2</sub> CH <sub>3</sub>	25	51	—
	PVTCA	25	—	53

<sup>a</sup>Contribution (%) of (3a) to the total rate of radical formation.

The occurrence of (3b) with nickel derivatives is consistent with the observations of Yoshisato and Tsutsumi<sup>5</sup>. These workers showed that β-epoxy ketones are formed in good yield (50–80%) by reaction of nickel carbonyl with α-bromo ketones at 30° in *N,N*-dimethylformamide solution. The results we have outlined lead to the following proposals for the mechanism of this reaction. We suggest that, in a typical case, the electron transfer reaction, equivalent to (3b), is:



Addition of the anion (III) to the carbonyl group of a second molecule of the α-bromo ketone, and cyclisation complete the reaction.



In our laboratories Dr. Go Hata has demonstrated that the system α-bromoacetone + Ni[P(OPh)<sub>3</sub>]<sub>4</sub> is an effective initiator for the polymerization of methyl methacrylate.

The mechanism we have suggested is clearly able to account for the formation of a  $\beta$ -epoxy ketone and the simultaneous initiation of free-radical polymerization (by bromine atoms).

The observation that, of the organometallic compounds studied, only derivatives of nickel give rise to reaction (3b) would appear to indicate that the anion  $X^-$  derived from trichloroacetates readily associates (presumably as an enolate ion) with nickel but not with molybdenum manganese and platinum. The ion (III) (equation (4)) probably behaves in a similar way. On the other hand the ion  $Cl_3C^-$  may not associate with the metal sufficiently strongly to facilitate (3b) when carbon tetrachloride is used as halide.

#### REFERENCES

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