The effects of different organic halide activators in vinyl polymerization using metal carbonyl initiators

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(Z. Naturforsch. **17 b**, 804—806 [1962]; eingegangen am 16. August 1962)

The relative efficiencies of 26 organic halogen compounds when used with the carbonyls of Cr, Mo, W, Mn, Fe and Ni for initiating the free-radical polymerization of methyl methacrylate are assessed; many active systems are found. Previous observations suggesting that the presence of the $-\text{C}(\text{hal})_3$ group is especially favourable are confirmed, although fluorine and iodine derivatives show no special activity. Outstandingly effective halides for initiating with the carbonyls of the Group VI metals are $\text{CCl}_3\text{CONH}_2$, CCl_3COOH , CCl_3CN and those incorporating aromatic rings, with the exception of $3-\text{F}\cdot\text{C}_6\text{H}_4\cdot\text{CCl}_3$ with $\text{Cr}(\text{CO})_6$.

In previous work on the use of metal carbonyls and their derivatives together with organic halides as free radical sources for the initiation of vinyl polymerization, we have chiefly been concerned with the detailed kinetic behaviour¹⁻⁶, and with the stereoregulating properties of the systems⁷. Generally, the halide used in conjunction with the carbonyl has been carbon tetrachloride, although the system $\text{Ni}(\text{CO})_4 + \text{CBr}_4$ has also been studied⁶. We have also examined the behaviour of a few different halides with the carbonyls of Cr, Mo and W². These experiments have now been extended; in this paper we describe a general survey of the field, made partly with the object of discovering active carbonyl-halide combinations. Although we have found many of these, it would be premature at this stage to formulate any general theory relating halide activity to structure. The results apply only to the polymerization of methyl methacrylate; we have indications of significantly different behaviour with other monomers, especially acrylonitrile.

Experimental

Materials

Metal carbonyls were obtained from the following sources:

Chromium hexacarbonyl: Diamond Alkali Company, Painesville, Ohio.

Molybdenum and tungsten hexacarbonyls: Climax Molybdenum Company, New York.

Manganese carbonyl, $\text{Mn}_2(\text{CO})_{10}$: Ethyl Corporation, Detroit.

These compounds were purified by sublimation at about 40 °C under high vacuum.

Nickel tetracarbonyl and iron pentacarbonyl: International Nickel Company (Mond) Ltd. These were purified by fractional distillation.

Halide compounds were research grade samples obtained from B.D.H. Ltd., and other commercial sources, and, where possible, were distilled before use.

Methyl methacrylate was purified by washing with 20% w/v aqueous sodium hydroxide to remove inhibitor, dried over CaCl_2 , and fractionated at reduced pressure. It was then partially polymerized by heating to 100° for 1 hour, and the residual monomer distilled off in vacuum immediately before use.

Methods

Monomer, carbonyl and halide were mixed under inactive (sodium) light and carefully degassed in vacuum. The tubes were then sealed off and heated. The polymers were precipitated into methanol, filtered, redissolved in CHCl_3 , reprecipitated into methanol, dried and weighed.

Results and Discussion

The yields of polymethylmethacrylate obtained by heating the monomer with the carbonyl-halide initiator under standard conditions are given in the table.

In all the metal carbonyl-halide systems previously studied^{1, 2, 4, 5, 6} it has been found that the

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¹ C. H. BAMFORD and C. A. FINCH, Proc. chem. Soc. [London] **1962**, 110.

² Idem., Proc. Roy. Soc. [London] **268 A**, 553 [1962].

³ Idem., Z. Naturforsch. **17 b**, 500 [1962].

⁴ Idem., Trans. Faraday Soc., in course of publication.

⁵ Idem., *ibid.*, in course of publication.

⁶ Idem., *ibid.*, in course of publication.

⁷ C. H. BAMFORD, M. S. BLACKIE and C. A. FINCH, Chem. and Ind. **1962**, 1763.

rate of polymerization is low in the absence of halide but increases rapidly with increasing halide concentration; the rate soon reaches a limiting value and further addition of halide then has little effect. The limiting rate has always been reached for $[\text{halide}] < 0.1 \text{ mole l.}^{-1}$ and we shall assume that this holds in the present systems. The concentrations of halides used were considerably in excess of 0.1 mole l.^{-1} . We shall also assume that the reactions resemble in mechanism those already investigated.

The simplest general mechanism has the following relevant steps under conditions of effectively zero carbon monoxide pressure.

Here M, $\text{Me}_m(\text{CO})_n$, $\text{C}(\text{hal})_3\text{X}$ represent the monomer, metal carbonyl and halide respectively, and $\text{R} \cdot$ the primary radical formed by the interaction which initiates polymerization. The velocity coefficients are numbered to conform with earlier work. At high halide concentrations the backward reaction in (1 a), and (1 b) become unimportant compared to (1 c) and the rate of formation of (II) is equal to the rate of the forward reaction in (1 a). It is therefore clear that the rate of initiation of polymerization J, (i. e. $k_4[\text{II}]$) is given by

$$J = \frac{k_1 k_4 [\text{M}] [\text{Me}_m(\text{CO})_n]}{k_4 + k_4''} \quad (2)$$

The variations in yield given in Table 1 can arise either from changes in J or from varying degrees

Halide \ Carbonyl	Cr(CO) ₆	Mo(CO) ₆	W(CO) ₆	Mn ₂ (CO) ₁₀	Fe(CO) ₅	Ni(CO) ₄
blank	2.8	1.1	2.0	0.5	5.9	0
Cl ₃ C—	6.2	6.8	3.1	9.4	5.2	19.6
—H	3.5	9.2	4.1	10.6	7.2	20.4
—F	11.2	29.3	10.4	26.5	49.7	100
—Br	13.1	51.2	13.5	17.7	0.2	48.9
—CHO	13.2	33.8	6.5	—	—	—
—CONH ₂ *	27.2	96.5	12.2	—	—	—
—CH ₂ Cl	6.7	11.9	8.6	—	49.8	68.0
—NO ₂	0.8	12.3	1.7	—	—	—
—COOH*	18.1	92.5	8.5	—	—	—
—CH ₃	4.4	9.0	4.4	—	5.4	25.7
—CHCl ₂	7.4	17.5	27.6	—	—	—
—CN	21.3	100	11.1	—	—	—
—CH ₂ OH	6.4	11.5	—	—	—	—
—CH(OH)OEt	18.0	44.8	8.6	—	—	—
—C ₆ H ₅	27.6	70.5	11.6	—	1.4	85.5
—C ₆ H ₄ F—3	3.9	76.2	8.9	—	1.1	83.2
—C ₆ H ₄ Cl—2	20.3	88.7	11.1	—	2.1	86.6
—C ₆ H ₄ Cl—4	19.8	68.3	14.2	—	1.3	85.6
—C ₆ H ₃ Cl ₂ *—2:4	22.0	93.2	2.1	—	3.3	87.7
—C ₆ H ₃ Cl ₂ —3:4	25.1	90.0	13.4	—	1.8	81.5
Cl ₂ CH—	—	—	—	—	—	—
—COOH	10.0	11.9	4.5	—	—	—
—CHCl ₂	3.0	6.0	4.0	—	—	—
—CN	11.2	67.0	7.8	—	—	—
Br ₃ C—	—	—	—	—	—	—
—H	14.8	32.8	—	—	—	—
—Br*	13.1	52.6	8.3	—	—	—
—CHO	0	1.9	0	—	—	—

Table 1. Dependence on halogen compound of metal carbonyl-initiated polymerization of methyl methacrylate at 100 °C. 9.5 ml. monomer were heated for 30 min. with 30 mg. carbonyl and 0.5 ml. of liquid or 0.8 g. of solid halogen compound. Solid compounds are marked by astrisks in the list. Percentage conversions are shown.

of retardation of the polymerization by the halide, or carbonyl, or some species formed by their mutual interaction. Retardation by the halides seems improbable except in the case of CCl_3NO_2 (nitro-compounds being well-known retarders⁹). Such information as exists in the literature on the other halides provides no reason for thinking they are effective retarders. Previous studies have shown that the carbonyls of Cr, W, Mn, Ni and possibly Mo do not retard the polymerization of methyl methacrylate appreciably, although they may act as inhibitors of the initiation by carbonyl-halide systems. The inhibition seems to be a function of the carbonyl concentration only, and does not depend on the halide concentration. No indication of significant retardation by carbonyl+halide has been observed. However, $\text{Fe}(\text{CO})_5$ has not been examined in detail and the possibility of retardation in systems containing $\text{Fe}(\text{CO})_5$ +halide must be borne in mind, especially since FeCl_3 is a powerful retarder on account of its ready reduction to FeCl_2 by polymethyl methacrylate radicals in non-aqueous solution⁹. This may apply to the low conversion obtained with $\text{Fe}(\text{CO})_5 + \text{CCl}_3\text{Br}$.

With these reservations in mind we may tentatively conclude that the majority of the results in the table reflect the prevailing values of J , the variations in conversion with a given carbonyl arising from changes in the ratio $k_4/(k_4 + k_4'')$ (equation (2)), since k_1 is not a function of the nature of the halide. This ratio depends on the relative ease with which complex (II) dissociates into radicals (1 d) or forms inactive products by reaction (1 e).

It is not possible to give a detailed discussion of the value of the ratio $k_4/(k_4 + k_4'')$ in terms of the halide structure since little is known of the chemistry of the competing reactions (1 d) and (1 e). Generally, any factor increasing the stability of the radical $\text{R}\cdot$ might be expected to favour a high value: e.g. $\cdot\text{C}(\text{hal})_3$ is more stable than $\cdot\text{C}(\text{hal})_2\text{H}$ and hence $\text{C}(\text{hal})_4$ should be a more effective halide than $\text{C}(\text{hal})_3\text{H}$. Similarly $\text{C}(\text{hal})_3\text{X}$ should be more active than $\text{C}(\text{hal})_2\text{X}_2$. This agrees with observation. Outstandingly effective halides for initiating with the carbonyls of the Group VI metals are $\text{CCl}_3\text{CONH}_2$, CCl_3COOH , CCl_3CN and those incorporating aromatic rings [with the exception of $3 - \text{F}\cdot\text{C}_6\text{H}_4\cdot\text{CCl}_3$ with $\text{Cr}(\text{CO})_6$].

Of the carbonyls of the group VI metals $\text{Mo}(\text{CO})_6$ is by far the most active initiator, with all the halides. We believe this implies that the complex (II) dissociates into radicals more readily in this case. The differences between $\text{Mo}(\text{CO})_6$ and the other carbonyls cannot satisfactorily be ascribed to greater inhibition by $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ (see also ref. (4)). Differences in the complexing behaviour of $\text{Mo}(\text{CO})_6$ compared to $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ have been observed in other connections¹⁰.

We have previously noted² that iodoform is not an active initiator with $\text{Cr}(\text{CO})_6$ or $\text{Mo}(\text{CO})_6$. Similar results have now been obtained with all the metal carbonyls in the table. In all cases some iodine is liberated and acts as a powerful retarder⁹. Negative results have also been obtained with carbonyls and RSiCl_3 compounds, probably on account of the relatively high Si-Cl bond energy¹¹.

⁸ C. H. BAMFORD and C. A. FINCH, unpublished results.

⁹ C. H. BAMFORD, W. G. BARB, A. D. JENKINS and P. F. ONYON, "Kinetics of Vinyl Polymerization", Chapter 6, Butterworths Scientific Publications, London 1958.

¹⁰ R. P. M. WERNER and T. H. COFFIELD, in "Advances in the Chemistry of the Co-ordination Compounds", ed. KIRSCHNER; Macmillan, New York 1961, p. 534.

¹¹ T. L. COTTRELL, "The Strengths of Chemical Bonds", Butterworths, Scientific Publications, London 1954, p. 257.