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Isobutylene Polymerization in the Presence of UV Light, Organic Iodides and Zinc Iodide

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Summary

Attempts have been made to adapt Kropp et al.'s finding(PIENTA, KROPP 1978) that adamantyl iodide in the presence of UV light produces carbocations to cationic polymerizations. Isobutylene polymerization did not occur upon UV irradiation with adamantyl iodide or tert.-butyl iodide alone, however low yields of polyisobutylenes were obtained in the presence of zinc dust and ZnI_2 ($I^{\ominus}$ complexors), respectively. The yield of polyisobutylene obtained with t-BuI/BCl_3 in the dark increased upon UV irradiation.

Introduction

In the presence of UV irradiation organic halides usually undergo homolytic cleavage and produce radicals (SAMMES 1973). In contrast, according to recent reports by Kropp et al. (KROPP et al. 1976), (PIENTA, KROPP 1978), certain organic bromides and iodides under similar conditions produce carbocations by heterolytic mechanism. Thus, upon extended UV irradiation in methanol 1-halonorbornanes and 1- and 2-adamantyl bromide and iodide and even 1-octyl iodide yielded products by nucleophilic substitution. The iodides were found to be more active than the respective bromides. Although radical processes still dominated, evidence for significant contributions by carbocationic products in all cases was demonstrated.

These observations prompted us to investigate the possibility of carbocationic polymerization initiation by carbenium ions generated from organic halides during

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UV irradiation. To minimize complications due to polymerizations induced by radicals we chose to study the polymerization of isobutylene at lower temperatures (this olefin cannot be polymerized by radicals). 1-Iodoadamantane and tert.-butyl iodide were selected as initiators. The adamantyl cation cannot eliminate a proton which was expected to facilitate the interpretation of results.

Concurrently with these investigations we studied the influence of light on isobutylene polymerization in the presence of ZnI_2, BCl_3 and BI_3.

Experimental

1-Iodoadamantane (AI) has been prepared (SCHLEYER, NICHOLAS 1961) and purified by repeated crystallization from ethanol, then dried under high vacuum at room temperature. t-Butyl iodide (t-BuI) was distilled twice over powdery molecular sieves (4Å) and then twice in high vacuum. Vacuum techniques, purification procedures, radiation conditions and polymer isolation have been described in detail (DIEM, KENNEDY 1977). In a typical experiment exact amounts of AI and zinc dust or zinc iodide were pumped down in a quartz reactor (18 cm long 2.3 cm diameter) under high vacuum for 5 hours. Charges of isobutylene and solvent distilled and sealed in the reactor were irradiated at -40^0 for 3.5 hours using a 450 W medium pressure mercury lamp 10 cm from the center of the reactor. In experiments using t-BuI and BCl_3 the charge was distilled into the reactor in high vacuum.

Results and Discussion

Preliminary results are presented in Table I. Polymer did not form upon irradiation of isobutylene, AI or t-BuI charges in bulk or in hexane solution (Expt. 1,2). Although large quantities of iodine and hydrogen iodide formed, probably by radical processes, these products do not induce isobutylene polymerization as found in separate experiments (Expt. 3,4). In several experiments zinc dust was used to scavenge iodine and minimize the effect of iodine on polymerization. Isobutylene polymerization in the presence of AI plus zinc dust gave low yield of polyisobutylene (Expt. 5). Diethyl zinc which is soluble in isobutylene had no influence (Expt. 6).

TABLE I

Effect of UV Irradiation on the Polymerization of Isobutylene (-40^0, 3.5h, Hanovia 450 W UV Lamp)

Exp.	Initiator	$M\cdot10^2$	Co-agent	$M\cdot10^2$	iC_4H_8 M	Yield, % Darkness	Yield, % UV Light
1	AI	2.4	-	-	11.7	0	0
2	t-BuI	1.7	-	-	1.7	0	0
3	I_2	9.7	-	-	11.7	0	0
4	HI	43	-	-	11.7	0	0
5	AI	5.0	Zn	excess	11.7	0	1.0
6	AI	6.0	$ZnEt_2$	24.5	11.7	0	0
7	t-BuI	1.6	ZnI_2	1.5	1.7	0	2.4
8	t-BuI	1.7	ZnI_2 + Zn	0.55 excess	1.7	0	3.8
9	t-BuI	1.9	BCl_3	1.9	1.7	4.8 5.5	9.8 16.8
10	t-BuI	2.2	BI_3	2.1	2.0	0	0

Zinc iodide enhanced polyisobutylene yields in the presence of t-BuI (Expt. 2 and 7). In the additional presence of zinc dust (Expt. 8) polyisobutylene yields increased further. Zinc iodide which forms <u>in situ</u> from zinc and iodine may stabilize iodine counter ions, e.g., $I^- + ZnI_2 \rightleftarrows ZnI_3^-$ and thus prolong propagation.

BCl_3 gave polymer in darkness and in the presence of UV light, however, irradiation at least doubled polyisobutylene yield (Expt. 9). Polymerization in darkness may be due to unscavengable protic impurities (KENNEDY et al. 1977). It is possible that photolysis of BCl_3 produces $Cl^\cdot$ which in turn generates HCl and thus leads to increased yields. In contrast, <u>t</u>-BuI/BI_3 combination did not induce polymerization (Expt. 10).

Polyisobutylenes obtained in these experiments at -40^0 were of relatively low molecular weight, 12-14 x 10^3.

Et_2AlCl reacts quickly in darkness with AI and t-BuI and the product, probably Et_2AlI, rapidly polymerizes isobutylene. Separate experiments with Et_2AlI (Table II) showed that this compound in conjunction with AI effectively coinitiates isobutylene polymerization at -40^0 in darkness. On account of these results these aluminum compounds cannot be used to stabilize I^- by complexation.

TABLE II

The Effect of Temperature on Isobutylene Polymerization with 1-adamantyl iodide/diethylaluminum iodide. (Yields in % ; [AI] = 1.10^{-3}M [Et_2AlI] = 5.10^{-3}M [<u>i</u>C_4H_8]= 1M, CH_3Cl, Vol. = 20 ml under N_2)

Charge: Isobutylene + Et_2AlI	-40^0	-50^0	-60^0	-70^0
AI present	100	8.0	2.0	0.73
AI absent	5	2.6	0.8	0.15

According to these results carbocations arise from alkyl iodides under the influence of UV light and are capable to induce olefin polymerization. These results also substantiate Kropp's findings that heterolytic bond cleavage of certain alkyl halides upon irradiation occurs. Low cationic polymerization efficiency is a serious limitation of this method and is probably due to simultaneous predominance of radical generation. The fact that polymer was obtained only in the presence of AI plus Zn or ZnI_2 may be due to acceleration of initiation or delay of termination by ZnI_2.

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