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Effect of reaction conditions on the radical addition of perfluorohexyl iodide to vinyl acetate*

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Abstract

The radical addition of perfluorohexyl iodide to vinyl acetate to give an iodine-containing adduct has been studied under different conditions in order to define their influence on the reaction Experiments have been carried out varying parameters (molar ratio of reagents, weight percent of initiator, reaction time, temperature, oxygen removal) and studying the effects on the perfluoroalkyl iodide conversion and on the adduct yield From the experimental data obtained, the conditions required to optimize the adduct yield have been defined

Introduction

The radical addition of perfluoroalkyl iodides to unsaturated compounds can lead to interesting results depending on the reagents used [2–5]. The direct reaction product is an iodine-containing adduct.

$$R_FI + CH_2{=}CH{-}R \longrightarrow R_FCH_2{-}CHI{-}R.$$

Other compounds can form, for example by further addition of adduct to the unsaturated reagent or by polymerization of the latter:

$$R_F{-}CH_2{-}CHI{-}R + CH_2{=}CH{-}R \longrightarrow R_FCH_2CH(R)CH_2{-}CHI{-}R,$$

$$n\,CH_2{=}CH{-}R \longrightarrow -[CH_2{-}CH(R)]_n-.$$

Byproduct formation generally depends on the presence of excess unsaturated reagent [2], but also on other reaction conditions (*e.g.* reaction time, temperature). The radical addition of perfluorohexyl iodide to vinyl acetate, using azo-bis(isobutyronitrile) (AIBN) as an initiator, was investigated in order to define the optimal conditions to reduce byproduct formation and maximize the adduct yield. The effect of reaction conditions was established by varying the molar ratio of the reagents, amount of initiator, time and temperature of reaction.

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Experimental

Reagents

Perfluorohexyl iodide, supplied by Atochem, was of commercial grade quality. Vinyl acetate was purchased from Aldrich Chemical Co.; before use it was treated with potassium hydroxide to remove inhibitor (hydroquinone) and distilled under nitrogen. AIBN was a Janssen product.

Apparatus

The experiments were carried out in a 50 ml two-necked Pyrex glass vessel placed in a thermostated bath and fitted with an inlet tube connected to a manometer and a nitrogen line, and with an outlet drain tube. The reaction behaviour was followed by GLC analysis of samples periodically drawn from the reactor by the drain tube.

General procedure

The reaction apparatus was flushed with dry nitrogen and charged with 9 g (0.020 mol) of perfluorohexyl iodide and the corresponding amounts of vinyl acetate and AIBN, calculated according to the reaction conditions fixed for the experiment. It was then cooled in a dry-ice/isopropanol bath and flushed again by passing a slow stream of dry nitrogen for 3 min in order to remove dissolved oxygen, finally it was placed in the thermostated bath at the fixed temperature. A small pressure of nitrogen (30–40 mmHg) was maintained in order to facilitate the periodic withdrawal of the reaction mixture samples for GLC analysis.

Analysis

GLC analysis of the reaction mixture was carried out on a Perkin-Elmer Sigma 3 instrument (1 m × 2 mm stainless steel column packed with SE 30 on 100–120 mesh Chromosorb P; temperature programme: 80 °C for 3 min, 10 °C/min to 120 °C; He as gas carrier at 30 ml/min) connected to a Sigma 1 gas chromatographic system for quantitative evaluations; for compound identifications a C. Erba model MFC 500/QMD 1000 GC–MS spectrometer was used (30 m × 0.5 mm capillary fused silica column packed with PS 264; temperature programme: 70 °C for 1 min, 7 °C/min to 200 °C, this temperature for 1 min, 20 °C/min to 280 °C, He as gas carrier with 10 ml/min). Figure 1 shows typical chromatograms recorded on the two instruments

Analytical data were used to define the changes in conversion of the limiting reagent (perfluorohexyl iodide) when the operational conditions were modified. Conversion was calculated by the following equation:

$$X = [(M_i - M_t)/M_i] \times 100$$

where M_i and M_t are respectively the initial number of moles and those present at time t for perfluorohexyl iodide. M_i and M_t were calculated for each analysed sample by GLC internal standard methods [6, 7], using perfluoro-octyl iodide as internal standard.

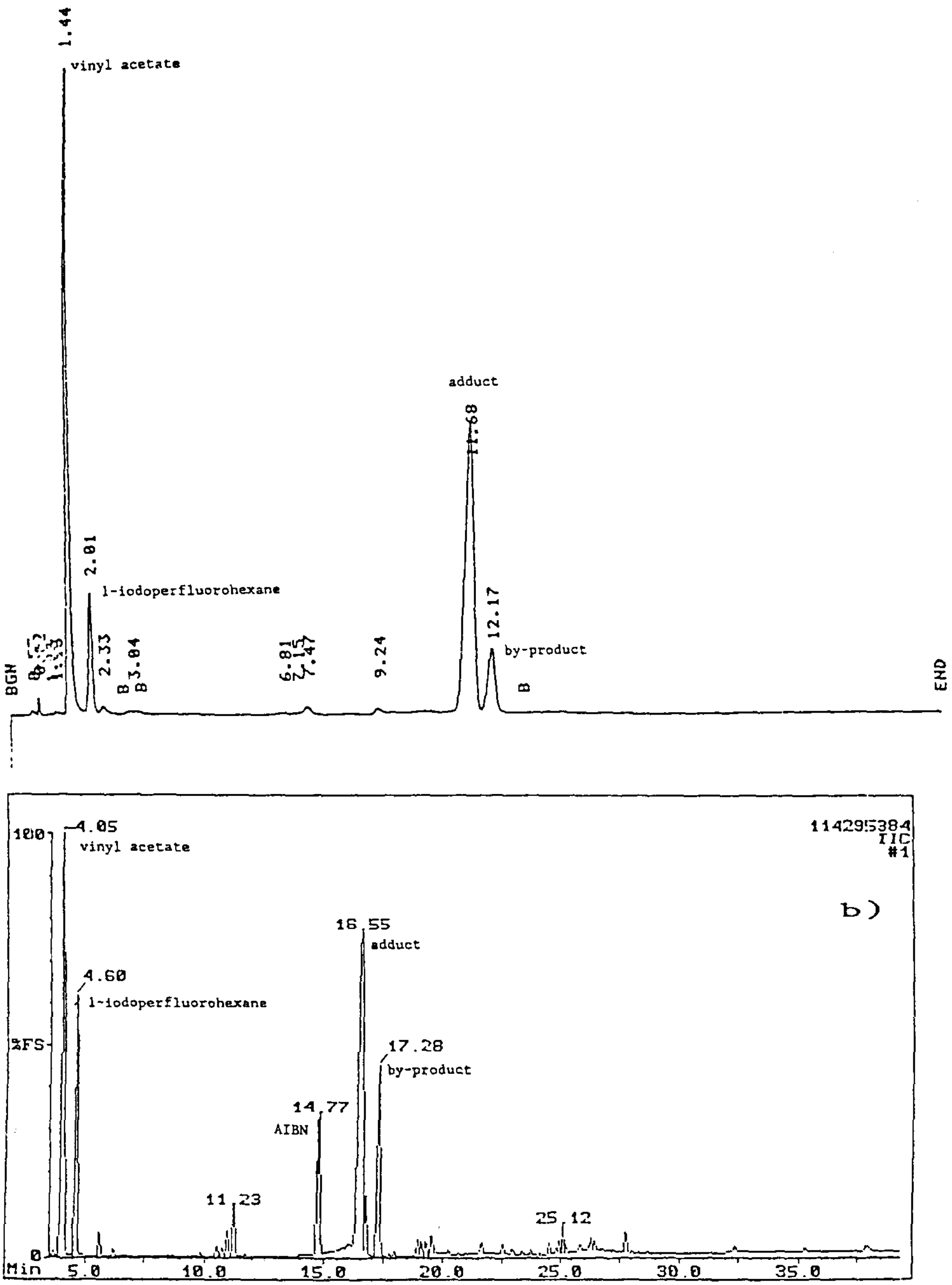

Fig. 1. Typical chromatogram of the reaction mixture recorded on Perkin-Elmer (a) or C. Erba (b) instrument.

Byproduct formation was considered in order to define the adduct yield. Telomer formation from vinyl acetate was not taken into account, because it did not involve the limiting reagent. Among the other byproducts only that which originated from perfluorohexyl iodide was considered, because it was quantitatively predominant (as can be seen in Fig. 1). This compound was identified by GC–MS analysis and was formed from addition of the iodine-containing adduct to vinyl acetate:

$$C_6F_{13}\text{-}CH_2\text{-}CHI\text{-}OCOCH_3 + CH_2{=}CH\text{-}O\text{-}COCH_3$$
$$\longrightarrow C_6F_{13}\text{-}CH_2\text{-}CH(OCOCH_3)CH_2\text{-}CHI\text{-}OCOCH_3$$

The MS data for adduct and byproduct are reported in Table 1.

TABLE 1

MS data recorded for byproduct [$C_6F_{13}CH_2CH(OCOCH_3)CH_2CHIOCOCH_3$] and adduct ($C_6F_{13}CH_2CHIOCOCH_3$)

Compound	*m/e*	Fragment	Relative intensity
adduct	473	$M^+ - C_2H_3O_2$	0.36
	453	$473 - HF$	0.95
	405	$M^+ - I$	0.08
	361	$405 - C_2H_4O$	0.71
	341	$361 - HF$	0.08
	314	$C_7F_{12}H_2$	0.16
	295	$C_7F_{11}H_2$	0.16
	213	$M^+ - C_6F_{13}$	0.08
	203	$473 - C_5F_{11}$	0.71
	169	C_3F_7	0.47
	141	CH_2I	0.79
	127	I	3.95
	119	C_2F_5	1.58
	100	C_2F_4	1.18
	69	CF_3	7.23
	43	C_2H_3O	100
byproduct	419	$M^+ - C_3H_4IO_2$	0.32
	405	$419 - CH_2$	2.92
	387	$405 - H_2O$	1.22
	361	$405 - C_2H_3O$	3.16
	340	$361 - HF$	2.09
	295	$C_7F_{11}H_2$	1.42
	213	$C_4H_6IO_2$	0.12
	195	$213 - H_2O$	0.10
	169	C_3F_7	0.59
	141	CH_2I	0.14
	127	I	0.39
	119	C_2F_5	3.56
	100	C_2F_4	0.91
	69	CF_3	9.09
	43	C_2H_3O	100

Since it was difficult to find a suitable compound to use as an internal standard for quantitative determination of the adduct and byproduct samples, the yields were evaluated by the ratio of their respective GLC areas as recorded on a Sigma 3 instrument. The recorded areas of two corresponding peaks were added to give a total area which was normalized to 100%; the ratio of each individual area to the total area gave the relative percentages of the corresponding compound.

Results and discussion

Experimental results are represented in the following diagrams.

Figure 2 shows how conversion changes with time and AIBN weight percent when the molar ratio vinyl acetate/perfluorohexyl iodide (MR) was 1 (Fig. 1a), 2.5 (Fig. 1b) or 5 (Fig. 1c). MR appears to be the predominant factor in achieving complete conversion of perfluorinated reagent, although the amount of AIBN is also important. In fact, when the reagents were in stoichiometric proportion (MR = 1), conversion was not complete despite a very high amount of AIBN (5%): the highest

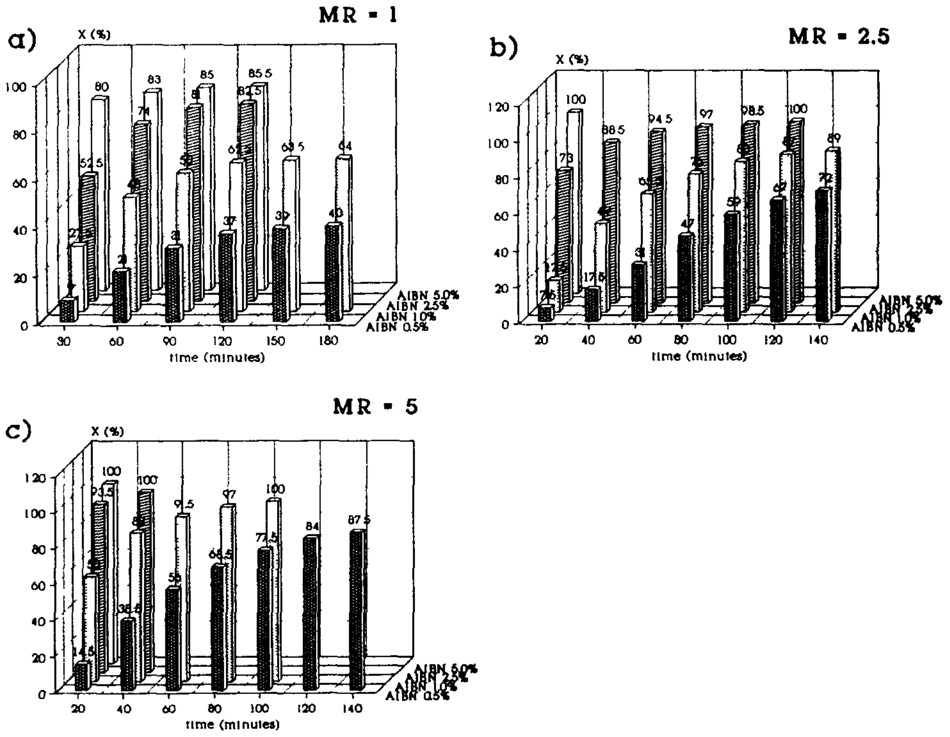

Fig 2 Effect of reaction conditions on 1-iodoperfluoro-n-hexane conversion

conversion observed was 86% after 120 min (Figure 1a). With MR = 2.5, conversion was already complete after 20 min with 5% AIBN, and only after 120 min. with 2.5% AIBN (Fig. 1b). Finally, with MR = 5, complete conversion could be obtained even with 1% AIBN after 100 min (Fig. 1c). Complete conversion was never observed with 0.5% AIBN. Furthermore it must be pointed out that with the amounts of AIBN used, the reaction times were very much shorter than those reported for analogous reactions [2, 3].

The importance of MR in the achievement of high conversions is confirmed by Fig. 3, in which the highest obtained conversions are plotted against MR and % AIBN. As can be seen, the maximum observed conversion increased with MR, even with the same amount of AIBN.

MR also appeared to be decisive for the adduct yield. In Fig. 4 the maximum observed relative percentages of adduct (P1) and byproduct (P2) are reported for each MR and % AIBN value. It can be seen that in

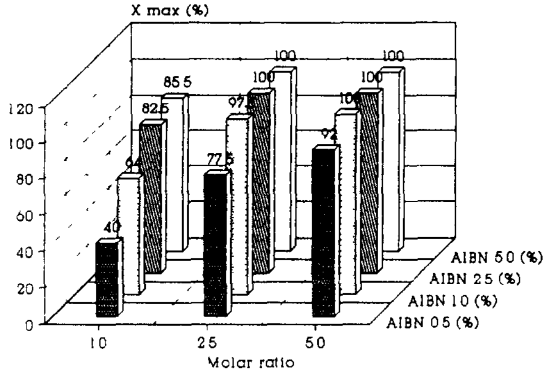

Fig 3 Influence of molar ratio of reagents and % AIBN on the maximum observed conversion

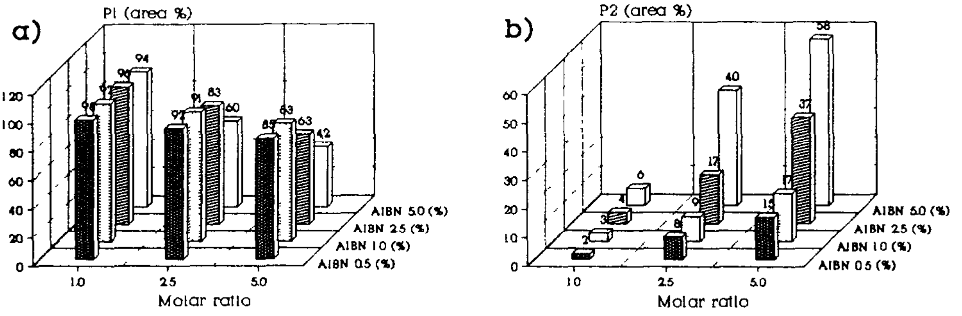

Fig 4 Effect of molar ratio of reagents and % AIBN on the formation of adduct (a) and byproduct (b)

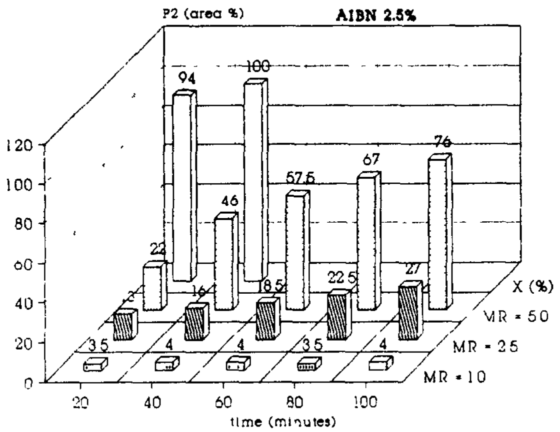

Fig 5 Influence of reaction time on the byproduct formation

the presence of excess vinyl acetate (MR > 1) the adduct formation decreased (Fig. 4a), while the byproduct yield increased (Fig. 4b). This effect was even more evident with higher amounts of AIBN; in fact, the highest yield of byproduct was observed with MR = 5 and 5% AIBN (Fig. 4b).

The reaction time also influenced byproduct formation (and thus the adduct yield). Figure 5 shows the relative byproduct percentages determined in experiments carried out with 2.5% AIBN at different values of MR, while prolonging the reaction after conversion was complete. As can be seen, the relative byproduct percentages increased with reaction time even when conversion was already complete. This effect was negligible with low values of MR, but was particularly marked with MR = 5; in fact, the relative byproduct percentage changed from 46% to 76% when the reaction was protracted for 60 min beyond the formal achievement of complete conversion. Byproduct formation when perfluorohexyl iodide had already been completely converted evidently rises from a further reaction of the adduct with the excess vinyl acetate.

The temperature effect on the reaction is shown in Fig. 6, where the values of conversion and relative byproduct percentage observed with different reaction temperatures are plotted. In order to make a significant comparison, the values obtained after 30 min of reaction have been considered. It can be seen that at 70 °C practically no reaction had occurred. On the contrary, at 90 °C a favourable effect could be observed, which was however balanced by marked byproduct formation.

Finally, Fig. 7 shows how conversion was improved by the removal of oxygen from the reaction environment. A predictable inhibiting effect of oxygen is evident, particularly at low MR values.

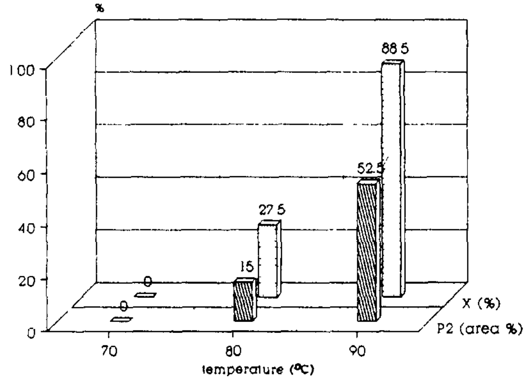

Fig 6 Influence of reaction temperature on conversion and byproduct formation

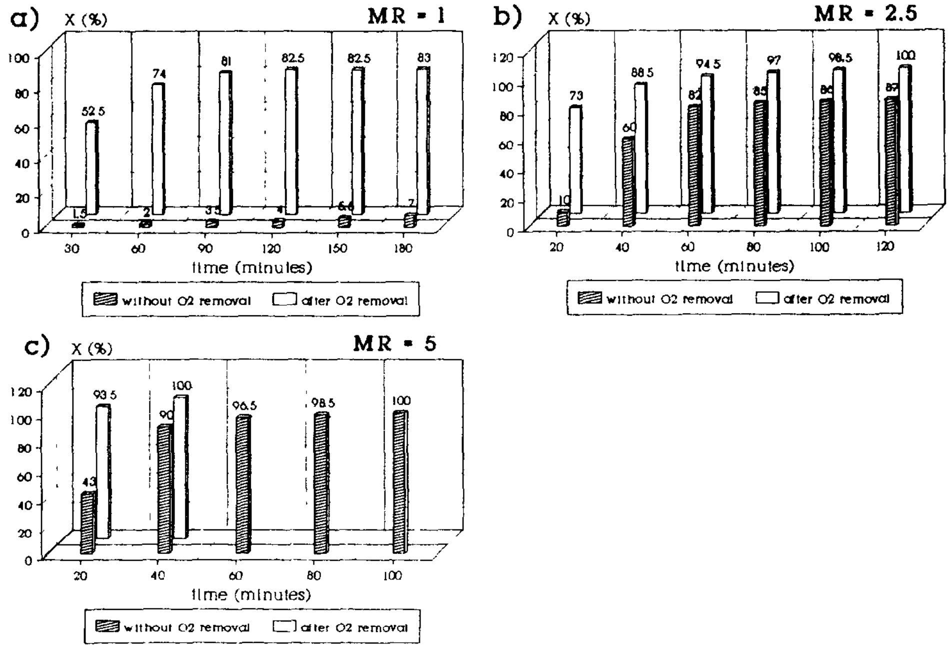

Fig 7 Effect of oxygen removal from reaction environment on conversion

Conclusions

From the reported experimental data, the following conclusions can be drawn:

- initiator: when % AIBN was increased either the reaction rate or the conversion increased, but byproduct formation was also enhanced;

- reagent molar ratio: an excess of vinyl acetate increased not only conversion but also the formation of byproduct, which in certain conditions even became the predominant product;
- reaction time: prolonged reaction times encourage the conversion of adduct into byproduct, particularly at high values of MR and % AIBN;
- temperature: temperatures over 80 °C had a favourable effect on conversion, but also resulted in byproduct formation.

On analysing these observations, two opposing requirements are found which are affected differently by the conditions of the reaction. On one hand, the reaction conditions should assure the complete conversion of perfluorohexyl iodide (which is the most expensive reagent); on the other hand, reaction conditions leading to high conversion also encourage byproduct formation, with a consequent drop in adduct yield. A compromise then appears unavoidable, considering that the main goal of the reaction is to change the greatest possible amount of perfluorohexyl iodide into adduct. From this point of view it is then advantageous to optimize yield rather than conversion.

Therefore to achieve this purpose, the following optimal reaction conditions can be fixed:
MR = 1;
AIBN = 2.5%;
temperature: 80 °C;
reaction time: 60–90 min.
Further oxygen removal from the reaction environment is necessary.

In these conditions, a conversion of ~80% can be obtained with negligible amounts of byproduct. The unreacted expensive perfluorinated compound can be recovered by distillation and recycled.

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