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# Diacetoxyiodobenzene and bis(Trifluoroacetoxy)Iodobenzene as Photoinitiators for Cationic Polymerisations

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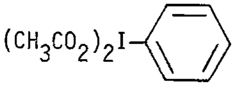
## Summary

It is shown that i-butyl vinyl ether, tetrahydrofuran, epichlorhydrin and cyclohexene oxide, which undergo typically cationic polymerisation, are polymerised by UV-irradiation in the presence of diacetoxyiodobenzene or bis(trifluoroacetoxy)iodobenzene.

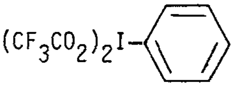
## Introduction

Recently the high efficiency of diaryliodonium salts, $Ar_2I^+X^-$, as photoinitiators for cationic polymerisations has been demonstrated (1). Although the mechanism of photoinitiation is certainly more complex (2) than originally proposed (1,3,4), it seems that two of the photodecomposition products of diaryliodonium salts are probably responsible for the initiation of the cationic polymerisation: the Brönsted acid HX (such as $HBF_4$) and mainly the transient phenyliodonium radical cation ($PhI^{+\cdot}$). An extension to other cationic polymerisations has been realised upon photolysis of benzoin derivatives in the presence of iodonium salts, through the generation of carbonium ions (5). Radical photopolymerisations with the system trisoxalato cobaltate-diphenyliodonium salts are also possible (6,7).

Because of the high reactivity of another class of hypervalent iodine compounds, i.e. diacyloxyiodoarenes, $(RCOO)_2IAr$, which react with a variety of substrates either homolytically or heterolytically (8), it was of interest to examine whether such compounds could also initiate photochemically cationic polymerisations. The chemical versatility of diacetoxyiodobenzene and bis(trifluoroacetoxy)iodobenzene, combined with their accessibility (both are commercially available and are also easily prepared), made them attractive candidates for this purpose and in this communication we report preliminary results which demonstrate their efficiency.



diacetoxyiodobenzene



bis(trifluoroacetoxy)iodobenzene

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## Experimental

All monomers and solvents used were purified by conventional drying and distillation procedures. The photoinitiators diacetoxyiodobenzene, bis(trifluoroacetoxy)iodobenzene and also p-chlorodiphenyliodonium iodide have been synthesised according to standard methods (8,9). The polymerisations were performed in the presence of atmospheric air at 20 °C. Samples of the monomer containing catalytic amounts of the photoinitiator were placed in Pyrex tubes and irradiated for 1 h, placed at a distance of 10 cm from the UV source (a Philips 400 W low pressure mercury lamp). Other experimental conditions are given in the Table. The polymers formed were precipitated by addition to the reaction mixture of a suitable solvent: methanol for i-butyl vinyl ether and diethyl ether for the other monomers. The intrinsic viscosities were measured with an Ubbelohde viscosimeter at 25 °C, in $CH_2Cl_2$.

## Results and Discussion

The following monomers have been found to polymerise upon UV-irradiation in the presence of diacetoxyiodobenzene or bis(trifluoroacetoxy)iodobenzene: tetrahydrofuran, epichlorhydrin, cyclohexene oxide and i-butyl vinyl ether. Detailed results with yields and intrinsic viscosities for i-butyl vinyl ether appear in the Table. For comparison some results with p-chlorodiphenyliodonium iodide ($p\text{-}ClC_6H_4I^+C_6H_5\ I^-$) have also been included, to demonstrate that diacetoxyiodobenzene and bis(trifluoroacetoxy)iodobenzene are at least equally effective concerning both polymer yields and viscosities. By changing the solvent from aliphatic (methylene chloride) to aromatic (benzene) an increase in yields and viscosities has been noted. A further increase occured when anisole was used as co-solvent.

TABLE

Photoinitiated Polymerisation of i-Butyl vinyl ether[a]

| Photoinitiator[b] | Solvent (ml) | Yield[c] (%) | [η] (dl/g) |
|---|---|---|---|
| DAI | $CH_2Cl_2$(8) | 32 | 0.14 |
| DAI | $C_6H_6$(8) | 38 | 0.17 |
| DAI | $CH_2Cl_2$(8)+anisole(0.5) | 62 | 0.24 |
| BTI | $CH_2Cl_2$(8) | 35 | 0.21 |
| BTI | $C_6H_6$(8) | 43 | 0.27 |
| BTI | $CH_2Cl_2$(8)+anisole(0.5) | 58 | 0.31 |
| CDII | $CH_2Cl_2$(8) | 35 | 0.15 |
| CDII | $C_6H_6$(8) | 41 | 0.23 |

[a] The quantity of the monomer was 0.02 mol.

[b] The quantity of each photoinitiator was 0.0004 mol. Abbreviations used are:DAI, diacetoxyiodobenzene; BTI, bis(trifluoroacetoxy)iodobenzene; CDII, p-chlorodiphenyliodonium iodide.

[c] Yields refer to 1 h of irradiation.

These results are to be contrasted with non-photochemical reactivity of diacetoxyiodobenzene and bis(trifluoroacetoxy)iodobenzene, which add their acyloxy groups to ethylenic double bonds (9,10) and oxidise epoxides (11) and ethers (12) to give a variety of products.

The lack of systematic studies on the photolysis of diacyloxyiodoarenes make at this point mechanistic discussions premature. However, even these preliminary results suggest that a single mechanism could hardly give a satisfactory explanation. By analogy with results obtained by laser-photolysis of diaryliodonium salts (2,13), it appears that besides formation of acetic or trifluoroacetic acid the highly reactive phenyliodinium radical cation may be formed and be mainly responsible for the initiation of the photopolymerisations. This species and the acids can arise according to the equations,

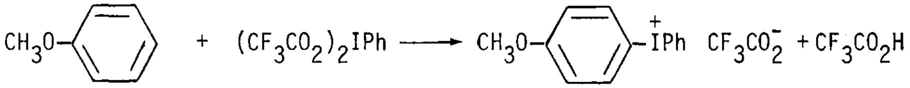
$$(RCO_2)_2IPh \xrightarrow{h\nu} RCO_2^{\cdot} + RCO_2I^{\cdot}Ph$$

$$RCO_2I^{\cdot}Ph \longrightarrow PhI^{+\cdot} + RCO_2^{-}$$

$$RCOO^{\cdot} \xrightarrow[-S^{\cdot}]{SH} RCOOH,\ RH,\ RR,\ CO_2$$

(SH, solvent or monomer)

That the role of acid produced is of limited importance has been demonstrated by irradiation of diacetoxyiodobenzene in $CH_2Cl_2$ and in $C_6H_6$. This resulted in its complete decomposition, with gas evolution, (probably a mixture of $CO_2$, $CH_4$ and $CH_3CH_3$), as it has been observed in its thermolysis, which follows a homolytic pathway (14). Acetic acid was also produced but only in 11% (in $CH_2Cl_2$) and 32% (in $C_6H_6$) yield. Therefore the small differences in yield and viscosity by changing the solvent can not be attributed to the amount of acid produced. Similarly, the nature of the acid coming from diacetoxyiodobenzene and bis(trifluoroacetoxy) iodobenzene, i.e. acetic and trifluoroacetic acid, respectively, is not significant. The effect of added anisole, however, is substantial and may be due to formation of a p-methoxydiphenyliodonium salt. Indeed, it is known that bis(trifluoroacetoxy)iodobenzene and anisole react at room temperature in this way (12), i.e.



Clearly, detailed investigations of the scope of these photoinitiated polymerisations as well as of their mechanisms are needed and will be undertaken.

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