Polymer Bulletin 6, 647-651 (1982)

Polymer Bulletin

Head Additon of Radicals to Methyl Methacrylate

Matthew J. Cuthbertson, Graeme Moad, Ezio Rizzardo, and David H. Solomon

Division of Applied Organic Chemistry, C.S.I.R.O.,
G.P.O. Box 4331, Melbourne, Victoria, Australia 3001

Summary

Contrary to a recent report, radicals produced from benzoyl peroxide and diisopropyl peroxydicarbonate react with methyl methacrylate mainly by addition to the less substituted end of the double bond (tail addition). Benzoyloxy radicals do give head addition, but only to a small extent relative to tail addition (ratio 5:66). With both initiators hydrogen abstraction from monomer is only a minor process ($\leqslant 1\%$). These results were obtained by analysis of the products formed when radicals are trapped by nitroxides.

Introduction

A recent communication appearing in this journal (KAMACHI *et al.* 1981) reported the results of spin-trapping experiments which, it was suggested, showed that the radicals formed from decomposition of diisopropyl peroxydicarbonate (IPP), benzoyl peroxide (BPO), and azobisisobutyronitrile (AIBN) react with methyl methacrylate (MMA) and methyl tiglate to give predominantly addition to the more substituted end of the double bond (head addition*). This result is contrary to what is expected on the basis of available data on free radical addition to olefins (CITTERIO *et al.* 1982, RUCHARDT 1980, TEDDER and WALTON 1980) and, in particular, it refutes previous observations that radicals derived from the above-mentioned initiators react with MMA to give exclusively tail addition (KUNITAKE and MURAKAMI 1974).

The appearance of these conflicting accounts prompts us to make a preliminary report of our own findings regarding the selectivity of the reactions of isopropoxycarbonyloxy and benzoyloxy radicals with MMA. We also offer an alternative explanation for the EPR spectra obtained by Kamachi *et al.* (1981).

Recently we have developed a new technique for quantitatively assessing the selectivity of the reactions of free radicals with vinyl monomers (RIZZARDO and SOLOMON 1979). The method is particularly suited to the study of

---

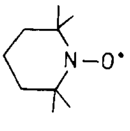
* Kamachi *et al.* (1981) use the term "tail addition" to describe this process.

0170-0839/82/0006/0647/$ 01.00

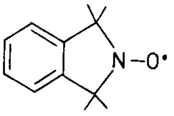
oxygen centred radicals and involves a product analysis of the decomposition of a free radical initiator in monomer solution in the presence of a nitroxide radical scavenger. The products so formed are stable alkoxyamines, each of which can be readily isolated and identified. This feature provides our technique with a considerable advantage over the conventional spin-trapping method, the limitations of which are discussed in a recent review (PERKINS 1981). Our radical trapping technique has already been applied to demonstrate the initiation pathways for the systems di-*tert*-butyl peroxalate in acrylic monomers (GRIFFITHS *et al.* 1982) and BPO in styrene (MOAD *et al.* 1982).

Results and Discussion

The decomposition of IPP or BPO[*] in MMA in the presence of a nitroxide (either 1 or 2) affords a mixture of alkoxyamines which have been isolated by preparative HPLC and characterized by spectroscopic and analytical methods. The reaction with BPO at 60°C gives the benzoyloxy radical adducts **3a** and **4a**,[**] the phenyl radical adduct **3b**, and the hydrogen abstraction product 5 (ratio 66:5:28:<1). Depending on the nitroxide concentration used, a proportion of phenyl radicals may react directly with nitroxide to give the phenoxyamine **6**. The reaction with IPP at 35°C affords the isopropoxycarbonyloxy radical adduct **3c** and compound 5 (ratio 99:1). In both experiments the major products **3a-c** are derived from the trapping of the radicals formed by tail addition to MMA. The formation of compound **4a** from the reaction with BPO demonstrates that head addition by benzoyloxy radicals does occur. However, the analogous product from isopropoxycarbonyloxy radicals **4b** is not observed and we must conclude that this radical does not give any significant amount of head addition. Hydrogen abstraction from the α-methyl of MMA (to give 5) accounts for only a very small proportion of total products with both initiators.



1

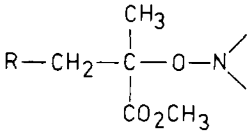


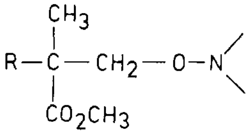
2

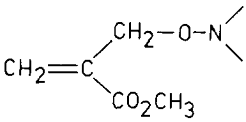
---

[*] Under the conditions of our experiments benzoyloxy radicals are formed mainly by a nitroxide-induced decomposition of BPO. The mechanism of this reaction is discussed elsewhere (MOAD *et al.* 1981). A similar situation applies with IPP.

[**] The compounds **3a** and **4a** obtained using nitroxide 1 as trapping agent are distinguished by their ^{1}H NMR spectra ($CDCl_3$) which show for **3a**: δ 4.50 (s, 2H, $-C\underline{H}_2O_2CPh$); and for **4a**: δ 4.16 (s, 2H, $-C\underline{H}_2ON<$).







5

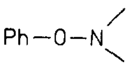
3a R = $PhCO_2$

b R = Ph

c R = i-Pr OCO_2

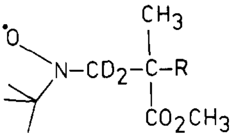
4a R = $PhCO_2$

b R = i-Pr OCO_2

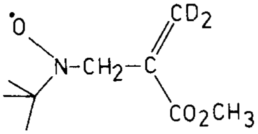


6

Kamachi *et al.* (1981) have examined the EPR spectra of the spin adducts produced when IPP or AIBN are heated with 2-methyl-2-nitrosopropane (MNP) at 30°C in MMA-β-d_2 solution. The spectra obtained consist of a 3-line spectrum (a_N=15G) superimposed on a 15-line spectrum (a_N=15G, a_D=1.5G). In the light of our findings it is highly unlikely that the 15-line spectrum is due to a radical of type 7 which would arise if the product of head addition to MMA-β-d_2 were trapped by MNP. The spectrum is nonetheless in accord with a nitroxide having an α-CD_2 substituent.

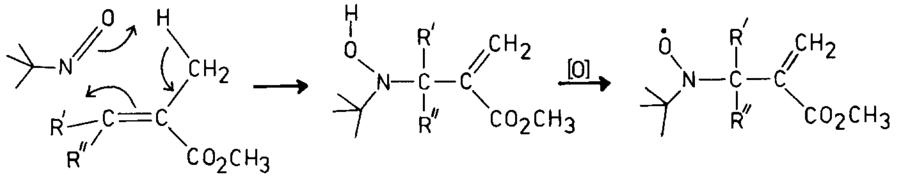


7



8

A possible explanation for the observed EPR spectra follows from the fact that olefins with allylic hydrogens react with nitroso-compounds (including MNP) *via* an ene reaction as shown below (MOTHERWELL and ROBERTS 1972, PERKINS 1981, SHENK and DE BOER 1979). Thus, the spectra obtained by Kamachi *et al.* (1981) are consistent with the radical **10a** which may be formed from the ene reaction between MNP and MMA-β-d_2 and subsequent oxidation of the hydroxylamine intermediate 9. This facile oxidation may be accomplished by the initiator or another molecule of the nitroso-compound (CHATGILIALOGLU and INGOLD 1981, PERKINS 1981). In accord with our proposal, we have found that a mixture of MNP and MMA (30°C, no added initiator) gives rise to an EPR spectrum consisting of a triplet of triplets (a_N=15.1G, a_H=10.3G) attributable to the nitroxide **10b**. A similar result had been reported for the reaction of MNP with MMA at 60°C, although



9 R′ = R″ = D

10a R′ = R″ = D

b R′ = R″ = H

c R′ = CH$_3$, R″ = H

the authors (KUNITAKE and MURAKAMI 1974) considered that **10b** arose *via* abstraction of a hydrogen from MMA by *tert*-butyl radicals formed from the thermal decomposition of MNP. However, in view of the recent work of Giese and Meixner (1977), who showed that *tert*-butyl radicals react primarily by tail addition to MMA, it is more likely that **10b** arises *via* the ene reaction described above. Any ambiguity could be resolved by examining the thermal reaction of MNP with MMA-β-d_2 at 60°C. The hydrogen abstraction reaction would produce radicals 8 and **10a**[*] while the ene reaction would give only **10a**.

More head addition is expected with methyl tiglate than with MMA since, on steric grounds, the α-methyl group of methyl tiglate should disfavour tail addition to some extent (CITTERIO *et al.* 1982). Nevertheless, it is also reasonable that methyl tiglate should react in a manner analogous to that proposed for MMA and give the radical **10c** *via* an ene reaction with MNP.

In conclusion, we emphasize that, although the initiation pathways observed with MMA are very much dependent on the nature of the initiating radical, in none of the cases examined thus far is head addition the dominant process. *tert*-Butoxy radicals react with MMA by abstraction from the α-methyl (32%) and from the ester methyl (5%) and by tail addition (63%) (GRIFFITHS *et al.* 1982, see also SATO and OTSU 1977). Benzoyloxy radicals react by tail (93%) and head (7%) addition and abstraction (<1%), while isopropoxycarbonyloxy and phenyl radicals give >98% tail addition. Available data suggest that a number of other radicals also give predominantly tail addition. These include: 2-cyanopropyl radicals (KUNITAKE and MURAKAMI 1974, SMITH and STEVENS 1972); *n*-hexyl, cyclohexyl, and *tert*-butyl radicals (GIESE and MEIXNER 1977, 1981); hydroxy radicals (FISCHER 1968); and phenylthiyl and benzoylthiyl radicals (SATO, ABE, and OTSU 1977, 1979)

---

[*] In this case the EPR spectrum would appear as 9-lines (due to 8) superimposed on 15-lines (due to **10a**).

References

CITTERIO, A., MINISCI, F., and VISMARA, E., J. Org. Chem., 47, 81 (1982)

CHATGILIALOGLU, C., and INGOLD, K.U., J. Amer. Chem. Soc., 103, 4833 (1981)

FISCHER, H., Adv. Polym. Sci., 5, 463 (1968)

GIESE, B., and MEIXNER, J., Chem. Ber., 110, 2588 (1977)

GIESE, B., and MEIXNER, J., Chem. Ber., 114, 2138 (1981)

GRIFFITHS, P.G., RIZZARDO, E., and SOLOMON, D.H., J. Macromol. Sci. Chem., 17, 45 (1982)

KAMACHI, M., KUWAE, Y., and NOZAKURA, S., Polym. Bull., 6, 143 (1981)

KUNITAKE, T., and MURAKAMI, S., J. Polym. Sci., Polym. Chem. Ed., 12, 67 (1974)

MOAD, G., RIZZARDO, E., and SOLOMON, D.H., Tetrahedron Lett., 22, 1165 (1981)

MOAD, G., RIZZARDO, E., and SOLOMON, D.H., J. Macromol. Sci. Chem., 17, 50 (1982)

MOTHERWELL, W.B., and ROBERTS, J.S., J. Chem. Soc., Chem. Commun., 329 (1972)

PERKINS, M.J., Adv. Phys. Org. Chem., 17, 1 (1981)

RIZZARDO, E., and SOLOMON, D.H., Polym. Bull., 1, 529 (1979)

RUCHARDT, C., Topics Current Chem., 88, 1 (1980)

SATO, T., ABE, M., and OTSU, T., Makromol. Chem., 178, 1951 (1977)

SATO, T., ABE, M., and OTSU, T., Makromol. Chem., 180, 1165 (1979)

SATO, T., and OTSU, T., Makromol. Chem., 178, 1941 (1977)

SCHENK, C., and DE BOER, TH. J., Tetrahedron, 35, 147 (1979)

SMITH, P., and STEVENS, R.D., J. Phys. Chem., 76, 3141 (1972)

TEDDER, J.M., and WALTON, J.C., Tetrahedron, 36, 701 (1980)

Accepted February 25, 1982