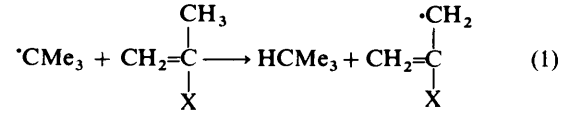
An Electron Spin Resonance Study of the Reaction between 2-Methyl-2-nitrosopropane and Methyl-substituted Vinyl Monomers

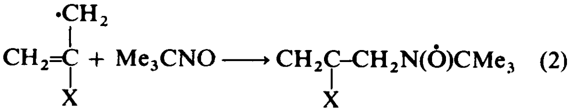
Jeremy Lane and Brian J. Tabner *
The Department of Chemistry, The University of Lancaster, Lancaster LA1 4YA

The reaction of 2-methyl-2-nitrosopropane with α-methyl-substituted vinyl monomers, such as α-methylstyrene and methyl methacrylate, gives rise to an e.s.r. spectrum (of the resulting adduct) showing two equivalent protons β to the $N(\dot{O})$ group. Two possible reactions leading to this adduct are (i) the 'ene' reaction and (ii) hydrogen-atom abstraction from the methyl group followed by trapping of the resulting radical by 2-methyl-2-nitrosopropane. Experiments employing the specifically labelled monomer methyl [β-$^2H_2$]methacrylate indicate that the 'ene' reaction is responsible for the observed e.s.r. spectrum.

There has been considerable recent interest in the spin-trapping technique as, in conjunction with e.s.r. spectroscopy, it leads to information concerning radicals normally present in low steady-state concentrations.[1] This latter condition applies to the various radical species present during the course of radical-initiated polymerisation, and some potential applications of the technique to the study of radical polymerisations have been explored.[2-4] However, it is well known that many *C*-nitroso compounds react with olefins, including those typically employed as monomers in polymerisation processes.[5-7] For example, Kunitake *et al.* observed primary and secondary e.s.r. spectra during the azobisisobutyronitrile-initiated polymerisation of methyl methacrylate in the presence of 2-methyl-2-nitrosopropane (MNP).[5] The primary spectrum was attributed to a trapped methyl methacrylate polymer chain $[\cdots{-}CH_2C(CO_2Me)MeN(\dot{O})CMe_3]$. However the second spectrum (a 1:1:1 triplet of 1:2:1 triplets) was also present when the initiator was omitted, and was attributed to a reaction between the monomer and the $^{\bullet}CMe_3$ radical formed by thermal decomposition of the trapping agent [reactions (1) and (2)].



$$^{\bullet}CMe_3 + CH_2{=}\underset{X}{\overset{CH_3}{C}} \longrightarrow HCMe_3 + CH_2{=}\underset{X}{\overset{\bullet CH_2}{C}} \qquad (1)$$



$$CH_2{=}\underset{X}{\overset{\bullet CH_2}{C}} + Me_3CNO \longrightarrow CH_2\underset{X}{C}{-}CH_2N(\dot{O})CMe_3 \qquad (2)$$

Support for hydrogen-atom abstraction from the methyl group [reaction (1)] was inferred when similar secondary spectra were observed in experiments involving other monomers with an α-methyl group such as methacrylic acid, α-methylstyrene, and methacrylonitrile, but not monomers such as styrene or methyl acrylate.

A secondary e.s.r. spectrum has also been observed independently by Sato *et al.* in experiments employing the same trapping agent and monomer but with di-t-butyl peroxylate as initiator.[6] These authors also proposed a hydrogen-atom abstraction similar to reaction (1), but suggested alternatively that the abstraction was a result of attack by the initiating radical.

Recently Mulvey and Waters have reported that 1,3,5-trichloro-2-nitrosobenzene reacts with a wide range of olefins in benzene solution to yield nitroxide radicals.[6] These olefins include stryene, buta-1,3-diene, and *trans*-stilbene. These workers proposed a reaction scheme involving the formation of a reactive diradical [reaction (3)], followed by several other

$$ArNO + CH_2{=}CHR \longrightarrow ArN(\dot{O})CH_2\dot{C}HR \qquad (3)$$

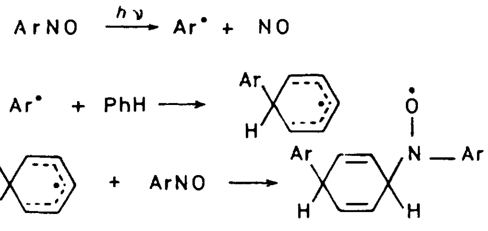
reactions including (4)—(6). However, in a recent publication

$$2\,ArN(\dot{O})CH_2\dot{C}HR \longrightarrow [ArN(\dot{O})CH_2CHR]_2 \qquad (4)$$

$$ArNO + ArN(\dot{O})CH_2\dot{C}HR \longrightarrow ArN(\dot{O})CH_2CHRN(\dot{O})Ar \qquad (5)$$

$$ArNO + ArN(\dot{O})CH_2\dot{C}HR \longrightarrow ArNHO^{\bullet} + ArN(\dot{O})CH{=}CHR \qquad (6)$$

Chatgilialoglu and Ingold have discussed the possibility of 'inadvertent photolysis' of the trapping agent in experiments in which visible light (natural or laboratory) is not rigorously excluded.[8] These workers conclude that many nitroso compounds do not form radicals in benzene in the dark, but do so readily if exposed to visible light. They proposed a reaction scheme (Scheme 1) involving reaction of the Ar$^{\bullet}$ radical derived from the nitroso compound with the solvent (benzene), and that it is this latter nitroxide which is often observed.



Scheme 1.

In a recent publication we have examined the radicals trapped by a variety of trapping agents during the course of the thermal decomposition of two common initiators of free radical polymerisations: benzoyl peroxide and azobisisobutyronitrile.[9] In this publication we report the results of our investigation of the reaction of a number of monomers, including a selection of those with an α-methyl substituent, with 2-methyl-2-nitrosopropane in benzene in which every possible precaution has been taken to exclude visible light.

Experimental

Materials.—Benzene (May and Baker) was purified as described in ref. 4 and dried over a Linde molecular sieve (4X). Styrene and methyl methacrylate (both B.D.H.) and α-methylstyrene (Aldrich) were all purified as described in ref. 10. 2-Methyl-2-nitrosopropane (MNP) (Lancaster Synthesis) was used as supplied and benzoyl peroxide was purified before use as described in ref. 4.

Methyl $[\beta\text{-}^2H_2]$methacrylate was prepared by reaction of methyl hydrogen methylmalonate with $[^2H_2]$formaldehyde in D_2O in the presence of diethylamine. The initial product was twice fractionated under nitrogen at reduced pressure and the isotopic purity of the final product was confirmed by ^1H and ^{13}C n.m.r. to be >98% (yield 27%). The methyl methylmalonate was prepared by the hydrolysis of dimethyl methylmalonate with NaOH in anhydrous methanol and the dimethyl methylmalonate was prepared from dimethyl malonate by reaction with methyl bromide in methanol.

Procedure.—Solutions of the monomers and of MNP in benzene were degassed using standard freeze–thaw procedures. The trapping agent and monomer were mixed immediately before sealing, under vacuum, in an e.s.r. sample tube. The concentration of MNP was 10^{-2} mol l^{-1} and those of the monomers were generally *ca.* 2.5 mol l^{-1}. All reactions were monitored, *in situ* in the e.s.r. spectrometer, at 333 K for at least 60 min. Every precaution was taken to exclude light at all stages. Despite these precautions, however, a spectrum of very low intensity, due to the formation of di-t-butyl nitroxide (produced by the photochemical decomposition of MNP) was sometimes observed. However, the spectrum obtained from the reaction of the spin-trap with the monomer, which grows steadily in intensity with reaction time, quickly dominated this spectrum.

Spectroscopic Measurements.—All e.s.r. spectra were recorded with a Varian E3 spectrometer with 100 kHz magnetic field modulation. Third-derivative spectra were recorded with the aid of a Telmore Instruments 100 kHz Subharmonic Generator. The magnetic field sweep was calibrated using Fremy's salt[11] and the temperature of the samples was controlled by means of a Varian E 4557 variable-temperature unit. Computer simulations of the experimental spectra were obtained using a Data General Nova computer on line to the e.s.r. spectrometer; hyperfine splitting constants quoted from these simulations are considered to be accurate to within ± 2 μT.

Results and Discussion

Methyl Methacrylate $[CH_2{=}C(CO_2Me)Me]$.—Figure 1(a) shows the e.s.r. spectrum obtained during the benzoyl peroxide-initiated polymerisation of methyl methacrylate in the presence of MNP in benzene in the dark. This spectrum is similar to that observed by Kunitake and Murakami during the azobisisobutyronitrile-initiated polymerisation of methyl methacrylate and arises from the superimposition of the spectra of two different nitroxides.[5] The third-derivative spectrum of the same sample, in which the broader line component is not observed [Figure 1(b)], confirms that the spectrum is due to a mixture of two nitroxides. This third-derivative spectrum is of interest as it also reveals the interaction of the unpaired electron with the protons of the CMe_3 group in the resulting nitroxide. The computer simulation of these spectra gives *a*(N) 1 495 and *a*(9H) 31 μT for the one nitroxide and *a*(N) 1 490 and *a*(2H) 960 μT for the other. Upon repeating the experiment in the absence of the initiator only the latter nitroxide is observed [see Figure 1(c)]. We therefore conclude that MNP reacts with methyl methacrylate to give a species of the general form $\cdot\cdot\cdot{-}CH_2{-}N(\dot{O})CMe_3$.

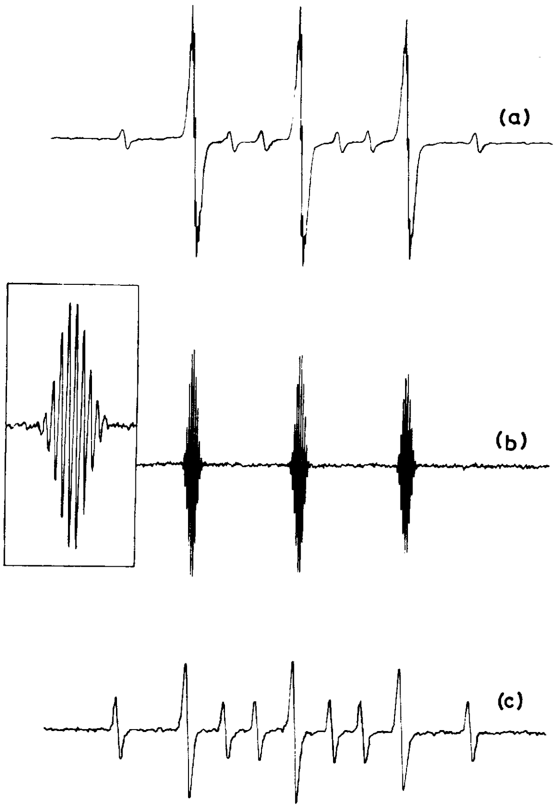
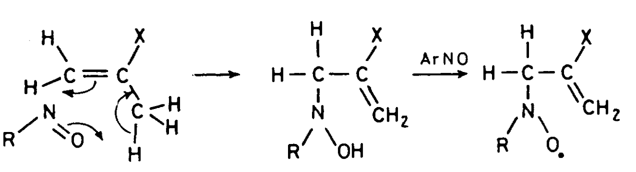


Figure 1. (a) The e.s.r. spectrum recorded during the benzoyl peroxide-initiated polymerisation of methyl methacrylate in the presence of 2-methyl-2-nitrosopropane in benzene. (b) The third-derivative spectrum of the same sample. The inset is a 3.5 × magnetic field expansion of the main low field absorption. (c) The e.s.r. spectrum recorded during the reaction between methyl methacrylate and 2-methyl-2-nitrosopropane in benzene

Clearly, in the absence of an inititator a radical cannot be formed from the monomer by classical initiation, or by abstraction of a hydrogen atom from the methyl group by the initiating radical. There remains, however, a possibility of hydrogen-atom abstraction from the methyl group by $^{\cdot}CMe_3$ radicals (formed by decomposition of MNP). However, this latter possibility appears unlikely as the small background spectrum of di-t-butyl nitroxide formed as a result of incomplete exclusion of light during sample preparation does not grow in intensity during these experiments. We therefore conclude that the thermal and photochemical decomposition of MNP to give $^{\cdot}CMe_3$ radicals is not significant. It appears, therefore, that the spectrum arises as a consequence of a reaction between the monomer and MNP. In order to explore this possibility we have studied the spectra formed from other monomers in the presence of MNP under the same conditions.

α-Methylstyrene $[CH_2{=}C(Me)Ph]$.—When the experiment in the absence of an initiator was repeated with α-methylstyrene, an e.s.r. spectrum was observed increasing in intensity with reaction time. This spectrum is similar to that obtained with methyl methacrylate, its computer reconstruction giving *a*(N) 1 485 and *a*(2H) 822 μT. It appears that a species having the general form $\cdot\cdot{-}CH_2{-}N(\dot{O})CMe_3$ has again been formed by reaction between the monomer and MNP. There remain two possible origins of such a species. It could be formed by hydrogen-atom abstraction from the methyl group by the trapping agent followed by the normal trapping reaction (2).



Scheme 2.

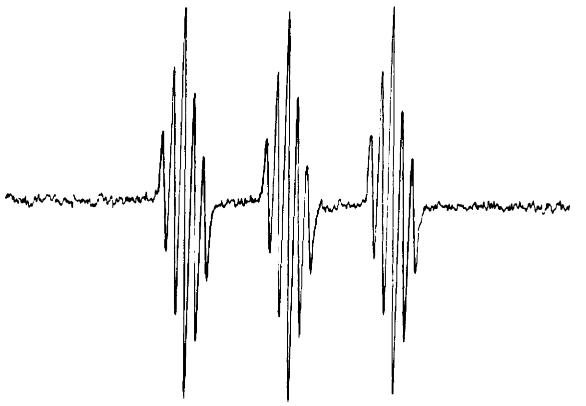


Figure 2. The e.s.r. spectrum recorded during the reaction between methyl [β-$^{2}H_{2}$]methacrylate and 2-methyl-2-nitrosopropane in benzene

Alternatively the spectrum could be obtained as a result of an 'ene' addition followed by subsequent oxidation of the hydroxylamine by MNP as proposed by Banks *et al.*[12] (Scheme 2).

Both the hydrogen-atom abstraction reaction and the ene addition reaction would be possible for both methyl methacrylate and α-methylstyrene. In order to distinguish between these two possibilities the experiment was repeated employing methyl [β-$^{2}H_{2}$]methacrylate.

Methyl [β-$^{2}H_{2}$]*Methacrylate* [$CD_2{=}C(CO_2Me)Me$].—Although the foregoing experiments indicate that an ene reaction might be occurring, the most satisfactory means of distinguishing between this and a hydrogen-atom abstraction from the methyl group of the monomer would be an experiment employing a specifically deuterium-labelled monomer. For this purpose methyl [β-$^{2}H_{2}$]methacrylate seemed an appropriate choice. With this monomer the hydrogen-atom abstraction reaction would give a nitroxide with two protons β to the $N(\dot{O})$ group [*i.e.* $\cdot\cdot$–$CH_2N(\dot{O})CMe_3$] whereas the nitroxide formed from the ene reaction would have two deuterons β to the $N(\dot{O})$ group [*i.e.* $\cdot\cdot$–$CD_2N(\dot{O})CMe_3$]. The e.s.r. spectrum obtained during the course of this experiment is illustrated in Figure 2 and clearly indicates the formation of the latter radical. The computer simulation of this spectrum reveals *a*(N) 1 486 and *a*(2D) 147 μT. A similar spectrum was observed by Kamachi *et al.* during the azobisisobutyronitrile-initiated polymerisation of methyl [β-$^{2}H_{2}$]methylacrylate together with another simple 1:1:1 triplet spectrum.[13] Kamachi *et al.* assumed that the former spectrum resulted following 'head' addition of the initiating radical to the monomer. However, in the light of our results it appears that this spectrum also arose from a product of the ene reaction between the monomer and the trapping agent, which would be occurring in addition to conventional 'tail' addition of the initiating radical to the monomer.

One would not expect a monomer without a methyl group to undergo either reaction, and we therefore investigated this possibility employing styrene as an example of such a monomer.

Styrene [$CH_2{=}CH(Ph)$].—Although no e.s.r. spectrum was expected during this experiment, a very weak spectrum was observed [*a*(N) 1 430 and *a*(H) 380 μT]. The origin of this spectrum is unclear. It could result from the addition of MNP to the monomer followed by the usual trapping reaction. However, styrene can undergo thermal self-polymerisation by a free radical process and the splitting constants observed in this experiment are fairly similar to those observed during the benzoyl peroxide-initiated polymerisation of styrene in the presence of 2-methyl-2-nitrosopropane.[2] The mechanism for the thermal generation of the initiating radicals from styrene has not yet been established, but the e.s.r. spectrum observed could result from species formed during this process.

Conclusion.—The foregoing series of experiments shows that methyl-substituted monomers will react with MNP in benzene in the dark although to differing extents. The spectra observed during these dark reactions are quite different from those observed in the presence of ordinary laboratory or natural light. The latter consist of simple 1:1:1 triplets [*a*(N) 1 512 μT] due to the formation of $(CMe_3)_2N(\dot{O})$ which under certain conditions can achieve sufficient intensity to obscure some of the spectra reported here. Secondary radicals are observed in the presence of light due to reactions of $^{\bullet}CMe_3$ with solvent and possibly also with the monomer. The radicals observed in our experiments do not originate from conventional radical polymerisation initiated by decomposition products derived from MNP. (In the absence of monomers, a spectrum corresponding to the formation of di-t-butyl nitroxide, formed following the possible thermal decomposition of MNP, does not become significant over the same time period as that employed in our experiments.) The foregoing experiments indicate that abstraction of a hydrogen atom from the methyl group of the monomer by MNP or by $^{\bullet}CMe_3$ radicals, formed as a result of decomposition of MNP, is not a significant reaction under the conditions employed; the results indicate that the ene mechanism is responsible for the formation of the observed radicals.

Acknowledgements

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