N-Phenylhydroxylamine as a Potent Initiator of Inhibited Hydrocarbon Autoxidation

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Summary *N*-Phenylhydroxylamine is a powerful catalyst of the autoxidation of squalene which has been inhibited by 2,6-di-t-butyl-*p*-cresol.

IN the course of mechanistic studies of the thermal decomposition of *N*-hydroxy-amines we have discovered that *N*-phenylhydroxylamine is a very active initiator of hydrocarbon autoxidation.

Thus, in the Figure is recorded the effect of low concentrations of *N*-phenylhydroxylamine on the rate of combination of gaseous oxygen at 100° with squalene inhibited by an excess of 2,6-di-t-butyl-*p*-cresol (8×10^{-2}M, in every case). It is readily perceived on comparing curves *b* and *c* with *d* that the hydroxylamine is of the same order of activity as the well known agent AIBN (αα′-azo-isobutyronitrile).

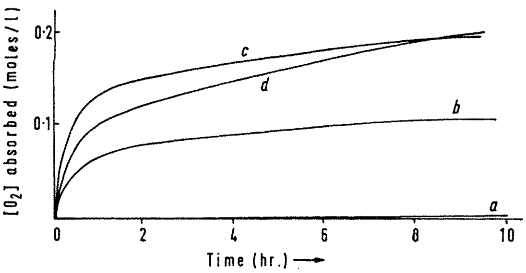

FIGURE. *Autoxidation of squalene inhibited by* 2,6-*di-t-butyl*-p-*cresol* (8×10^{-2}M) *at* 100° *and* 760 *mm. oxygen pressure, containing* (*a*) *no other additive,* (*b*) N-*phenylhydroxylamine* ($2{\cdot}3 \times 10^{-2}$M), (*c*) N-*phenylhydroxylamine* ($4{\cdot}1 \times 10^{-2}$M), (*d*) *AIBN* ($4{\cdot}6 \times 10^{-2}$M)

During the fast stage of oxygen absorption there becomes totally combined in the system approximately 4·0 moles of oxygen per mole of *N*-phenylhydroxylamine employed. This may be compared with available data[1] on the autoxidation of *N*-phenylhydroxylamine *per se* in methanol where *ca.* 0·25 moles of oxygen react per mole of the hydroxylamine in accordance with the stoicheiometry:

$$4\,\mathrm{PhNHOH} + \mathrm{O_2} \rightarrow 2\mathrm{PhN(O){=}NPh} + 4\mathrm{H_2O} \qquad \text{(i)}$$

There is therefore no doubt that our results indicate substantial oxidation of the hydrocarbon substrate.

For squalene/2,6-di-t-butyl-*p*-cresol/*N*-phenylhydroxylamine systems at 100° we also find the rates of autoxidation to be nearly directly proportional to oxygen pressure ($1{\cdot}32 \times 10^{-7}$ moles oxygen/litre of squalene/mm. oxygen pressure, for the phenol at 8×10^{-2}M and phenylhydroxylamine at $4{\cdot}1 \times 10^{-2}$M) indicating that molecular oxygen is involved in the rate-determining initiation step. Ogata *et al.*[1] have suggested that in methanolic solution the autoxidation of *N*-phenylhydroxylamine involves the reactions

$$\mathrm{PhNHOH} + \mathrm{O_2} \rightarrow \mathrm{Ph}\overset{+\,\cdot}{\mathrm{N}}\mathrm{HOH} + \mathrm{O_2}{\cdot}^{-} \qquad \text{(ii)}$$

$$\mathrm{PhNHO^{-}} + \mathrm{O_2} \rightarrow \mathrm{PhNHO}{\cdot} + \mathrm{O_2}{\cdot}^{-} \qquad \text{(iii)}$$

We believe that a closely related mechanism might also operate in the present hydrocarbon autoxidation initiation, and essentially we would accept that $\mathrm{HO_2}{\cdot}$ radicals probably set off the usual type of free radical-chain autoxidation of the squalene. It is interesting however that di-s-octyl *p*-phenylenediamine, which is also capable of losing electrons to molecular oxygen, is a relatively feeble initiator in place of *N*-phenylhydroxylamine in our inhibited squalene systems.

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[1] Y. Ogata, Y. Sawaki, J. Mibae, and T. Morimoto, *J. Amer. Chem. Soc.*, 1964, **86**, 3854, and references cited therein.