

Antioxygenic Effects of Some Nitroso Compounds. An Interpretation of the Effects from the Point of View of Resonance.

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It was shown by Carré and Peigné⁽¹⁾ that antioxygenic action seems to depend on the difference of the polarity of elements directly to antioxygenic substances. The authors have now examined several nitroso compounds for antioxygenic activity on the autoxidation of benzaldehyde exposed to atmospheric oxygen, since nitroso compounds have, in general, very large dipole moment. Their antioxygenic actions are, however, somewhat diverse. Some are very effective and some are not.⁽²⁾ Aliphatic nitroso compounds (such as nitroso-dimethylamine and nitroso-methylurethane) generally show no or very little retarding effect, while aromatic compounds show more or less strong activity.

Some examples of our experiments using nitrosobenzene, *p*-nitrosotoluene, *p*-chloro-, *p*-bromo- and *p*-iodo-nitrosobenzenes as antioxidants will be shown.

In a flask of 1370 c.c. volume, 5 c.c. freshly distilled benzaldehyde (5×10^{-2} mols) and the antioxidant (4×10^{-5} mols) are introduced. After standing for 24 hours the formed benzoic acid is titrated with alkali.

Antioxidant	Benzoic acid formed	Antioxidant	Benzoic acid formed
None	1.263 g.	<i>p</i> -Chloro-nitrosobenzene	0.074 g.
Nitrosobenzene	0.777 g.	<i>p</i> -Bromo-nitrosobenzene	0.069 g.
<i>p</i> -Nitrosotoluene	0.599 g.	<i>p</i> -Iodo-nitrosobenzene	0.018 g.

The experiments show that the order of the effects of the substituents is $I > Br > Cl > CH_3 > H$. This order is just coincident with the sequence of the *o,p*-directive forces of groups in aromatic substitution,⁽³⁾ which may be regarded as being determined by the electromeric effect of the radicals.⁽⁴⁾ The above results, therefore, indicates that the antioxygenic activity is likely to depend on the resonance of a nitroso compound, which is effected easily in the presence of conjugated double bonds as in the cases of aromatic nitroso compounds.

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(1) P. Carré and L. Peigné, *Compt. rend.*, **208** (1939), 108.

(2) Among nitroso compounds the following ones have been already examined on the autoxidation of benzaldehyde with the results: nitroso-methylurethane is almost inactive, but *p*-nitroso-dimethyl-aniline is very active. C. Moureu, C. Dufraisse and M. Badoche, *Compt. rend.*, **183** (1926), 823.

(3) A. F. Holleman, *Chem. Rev.*, **1** (1925), 187.

(4) On the electromeric effect of the methyl group see E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, **1940**, 949.