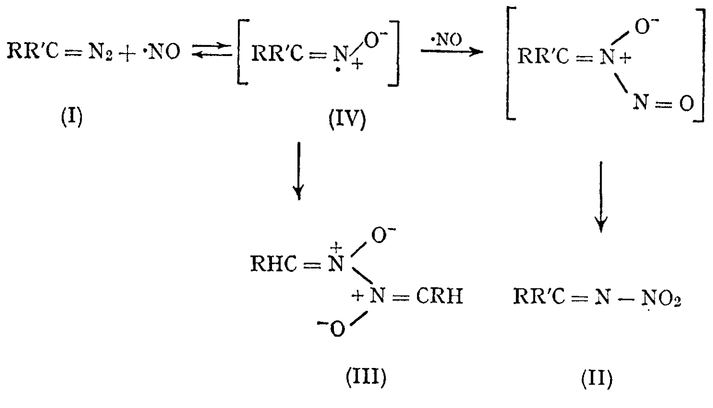
Formation of Nitroxyl (Iminoxy) Radicals in the Reaction of Nitrogen(II) Oxide with Diazo-compounds

By O. L. Chapman and D. C. Heckert

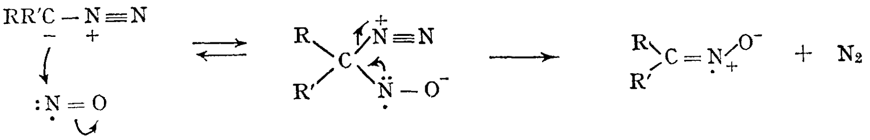
(*Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa*)

It has been reported that many diazo-compounds react with nitrogen(II) oxide in the dark to give nitrimines (II) and, in some cases, azine-bis-oxides (III).[1] The latter products are isolated only when one of the substituents on the diazo-compound is hydrogen (I, R = H).[1] It was postulated on the basis of product structure that the nitroxyl radical (IV) was an intermediate in this reaction.[1] No direct evidence was available for the formation of nitroxyl radicals and attempts to generate and observe nitroxyl radicals by thermal cleavage of the azine-bis-oxides were fruitless.[1]


(I) (IV) (III) (II)

We now wish to report direct observation of nitroxyl radical e.s.r. spectra in acetone solutions of diazo-compounds which have been saturated with nitrogen(II) oxide. Diphenyldiazomethane under these conditions gave rise to the nitroxyl radical derived (by one-electron oxidation) from benzophenone oxime. The e.s.r. spectrum of the radical was observed easily at room temperature (the lifetime was of the order of a few minutes) and was characterized by comparison of the splitting constants with those reported.[2] Methylphenyldiazomethane and phenyldiazomethane gave rise to known nitroxyl radicals which were shorter lived and which could be observed only at lower temperatures. Observation of the e.s.r. spectra of the nitroxyl radicals is in accord with Horner's postulate. Chemical evidence also supports the intermediacy of nitroxyl radicals in the formation of nitrimines and aldazine-bis-oxides.[3] Observation of e.s.r. spectra in the presence of nitrogen(II) oxide is somewhat surprising. It is feasible in this case because of the low solubility of the gas in acetone. Nitroxyl radical e.s.r. spectra have also been observed in the oxidation of oximes by nitrogen(II) oxide in acetone solution.[3]

The mode of formation of nitroxyl radicals from diazo-compounds is of some interest. The diazo-compounds are stable under the conditions of the experiment but rapidly evolve nitrogen when treated with nitrogen(II) oxide. It thus seems reasonable that carbenes are not intermediates (although carbene-derived products such as azines are observed in some of these reactions) in the formation of the nitroxyl radicals. It seems more reasonable that attack occurs directly on the diazo-compound as suggested earlier.[1]



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[1] L. Horner, L. Hockenberger, and W. Kirmse, *Chem. Ber.*, 1961, **94**, 290, and references therein cited.

[2] J. R. Thomas, *J. Amer. Chem. Soc.*, 1964, **86**, 1446; M. Bethoux, H. Lemaire, and A. Rassat, *Bull. Soc. chim. France*, 1964, 1985; B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1966, 86; B. C. Gilbert, R. O. C. Norman, and D. C. Price, *Proc. Chem. Soc.*, 1964, 234.

[3] O. L. Chapman and D. C. Heckert, unpublished observations.