

E-Radiation Chemistry of Diphenylpicrylhydrazyl (DPPH), II\*

E-Radiation Induced Nitration of DPPH by NO<sub>2</sub> Radicals

WERNER H. KALUS

Bundesforschungsanstalt für Lebensmittelfrischhaltung, Institut für Strahlentechnologie, Karlsruhe

(Z. Naturforsch. **29b**, 286–287 [1974]; eingegangen am 18. Oktober 1973)

Radiolysis, free radicals, radical scavengers

The radiation chemistry of simple nitro-alkanes has been investigated principally in the vapour phase<sup>2</sup>, but also in the liquid phase<sup>3</sup>; in all cases, the primary process is considered to be a homolytic cleavage of the carbon-nitrogen bond. ESR evidence for an alternative pathway in solution in-

volving intermolecular hydrogen abstraction and the formation of the radical RNO<sub>2</sub>H has recently been advanced<sup>4</sup>. Our studies of the e-radiation chemistry of dilute solutions of DPPH in nitrogen dioxide containing solvents such as nitromethane, nitrobenzene, and 95 atom % <sup>15</sup>N enriched nitrobenzene have revealed details which might shed some light on the chemical mechanisms of radiation induced nitration of the phenyl ring in DPPH. Both reactions provide convincing chemical evidence for C–N bond cleavage and for hydrogen abstraction.

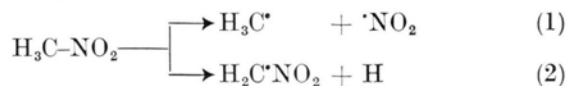
*p*-Nitro-diphenylpicrylhydrazine (NO<sub>2</sub>-DPPH<sub>2</sub>) and diphenylpicrylhydrazine (DPPH<sub>2</sub>) have been previously identified as major products of DPPH radiolysis in methyl iodide solution<sup>1</sup> and their presence has been confirmed in the present work. The 100 eV yields (G-values) of the different reaction products are given in Table I. For all runs a standard dose of 1 · 10<sup>21</sup> eV g<sup>-1</sup> was used.

Table I. Effect of solvents on the G-values of radiolytic products formed by e-radiolysis of DPPH (5 · 10<sup>-2</sup> mole/l).

Starting material	<sup>(15)</sup> NO <sub>2</sub> -DPPH <sub>2</sub>	DPPH <sub>2</sub>	G (Product)	
			<i>p</i> -( <sup>15</sup> )nitro-diphenylamine	2,4,6-trinitroaniline
DPPH/CH <sub>3</sub> NO <sub>2</sub>	2.6	3.2	0.5	0.3
DPPH/C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	2.2	1.5	0.3	0.2
DPPH/C <sub>6</sub> H <sub>5</sub> <sup>15</sup> NO <sub>2</sub>	2.0	1.4	0.2	0.2

The results of irradiations of DPPH in nitrobenzene at lower concentration (6 · 10<sup>-6</sup> mole/l) are summarized in Table II. The yields for the major product formation (NO<sub>2</sub>-DPPH<sub>2</sub> and DPPH<sub>2</sub>) show a dose dependence. In particular it can be seen that the nitration product was formed in significant amounts above 6 · 10<sup>20</sup> eV g<sup>-1</sup>. DPPH<sub>2</sub> was a major product below 4 · 10<sup>20</sup> eV g<sup>-1</sup> and decreased with increasing dose. At higher doses decomposition of NO<sub>2</sub>-DPPH<sub>2</sub> occurs forming degradation products as listed in Table I. The most probable explanation of these observations is that under the conditions of the experiment a nitration of the hydrazine (DPPH<sub>2</sub>) takes place.

The high yields of *p*-nitro-diphenylpicrylhydrazine and diphenylpicrylhydrazine indicate the importance of nitrogen dioxide free radicals and of H atoms as intermediates in the e-radiolysis of nitro-alkanes and aromatic nitro-compounds. By the action of high energy electrons on the solvent both processes, CH and CN bond cleavage, take place (1, 2).

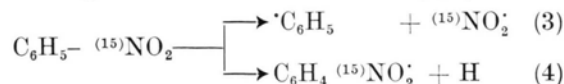


Sonderdruckanforderungen an Dr. WERNER H. KALUS, Bundesforschungsanstalt für Lebensmittelfrischhaltung, Institut für Strahlentechnologie D-7500 Karlsruhe, Engesserstraße 20.

Table II. e-Radiolysis of DPPH in nitrobenzene solution (6 · 10<sup>-6</sup> mole/l). Concentration dependence of NO<sub>2</sub>-DPPH<sub>2</sub> and DPPH<sub>2</sub> with radiation dose.

Starting material	Absorbed dose 10 <sup>20</sup> eV g <sup>-1</sup>	Products [weight %]	
		NO <sub>2</sub> -DPPH <sub>2</sub>	DPPH <sub>2</sub>
DPPH/C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	0.6	2.8	55.3
	3.1	19.8	30.2
	6.2	60.4	15.8
	9.4	73.1	3.7
	12.5	71.9	–

In the case of nitrobenzene and [<sup>15</sup>N]-nitrobenzene the mechanism of decomposition is assumed to be analogous to that of nitromethane (3, 4).

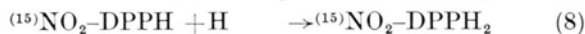
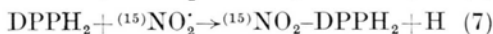
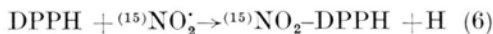


In all cases studied the simplest reaction between H and the free radical scavenger DPPH is addition to form the corresponding hydrazine (5).



The formation of the nitration product is an example where the substitution of NO<sub>2</sub> to DPPH or DPPH<sub>2</sub> by elimination of H is assumed to be the principal reaction following radiolysis of the solvents. The final reaction products will then be

formed by the various combinations of reactions (6-9).



From the low yield of degradation products it is assumed that chemistry arising from the cleavage of the N-N bond in the hydrazine  ${}^{(15)}(\text{NO}_2\text{-DPPH}_2)$  is of no more than minor importance in the production of [*p*- ${}^{(15)}\text{N}$ ] nitrodiphenylamine and trinitroaniline, since caging effects in the condensed phase would lead to preferential recombination of the radical pair. The scheme of reactions given in equations (1-9) is consistent with the experimental results.

### Experimental

DPPH (Schuchardt, München) was crystallized from  $\text{CS}_2$  and tested by t.l.c. on Polygram Sil S-HR Plates (Macherey-Nagel) for purity and no impurities were detected. Nitrobenzene and nitromethane, reagent grade (Merck), were fractionated

at reduced pressure, and the middle cut was used for the irradiation. [ ${}^{15}\text{N}$ ] nitrobenzene was a commercial sample, supplied by Fa. Roth (Karlsruhe). It contained 95 atom%  ${}^{15}\text{N}$  isotope and was used without purification.

The experimental techniques and dosimetry used in the present study are essentially the same as described in the preceding paper. The source of radiation was a Varian electron accelerator Typ V 7703 with variable beam energy 5-22 MeV. Samples approx. 5 ml of liquid containing DPPH, were degassed by the usual freeze, pump, and thaw technique, and then sealed off in special pyrex glass ampoules (15 ml). The unreacted solvent was removed under reduced pressure ( $10^{-3}$  torr) and the residual solids were separated by t.l.c. The yields of products were measured spectroscopically.

When [ ${}^{15}\text{N}$ ] nitrobenzene was used as a source of  ${}^{15}\text{NO}_2$  free radicals the 70 eV mass spectrum of [*p*- ${}^{15}\text{N}$ ] nitrodiphenylpicrylhydrazine showed the molecular ion  $\text{M}^+$  at  $m/e=441$ . The [*p*- ${}^{15}\text{N}$ ] nitrodiphenylamine ion at  $m/e$  215, produced by N-N bond fission of the molecular ion was observed to lose the label completely in the process  $(\text{M}-{}^{15}\text{NO}_2)^+ \rightarrow \text{C}_{12}\text{H}_{10}\text{N}^+$  ( $m/e=169$ ).

<sup>1</sup> W. H. KALUS, Z. Naturforsch. **27b**, 514 [1972].

<sup>2</sup> H. A. MORRISON, The Chemistry of the Nitro and Nitroso Groups, Part I, ed. H. Feuer, p. 165, Interscience, New York 1969.

<sup>3</sup> R. E. REBBERT and N. SLAGG, Bull. Soc. chim. Belges **71**, 709 [1962].

<sup>4</sup> C. CHACHATY and A. FORCHIONI, Tetrahedron Letters [London] **1968**, 1079.