

ESR EVIDENCE FOR THE INTERMEDIACY OF DIAZENIUM RADICALS IN
THE PHOTOLYSIS OF AZOESTERS

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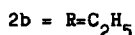
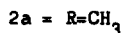
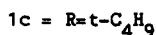
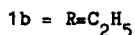
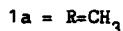
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Azoalkanes decompose on heating or irradiation into molecular nitrogen and alkyl radicals. Whether this reaction is concerted or proceeds via diazenium has been a matter of controversy in recent years,¹⁻⁷

In this paper we would like to present evidence which shows that the photo decomposition of azoesters is a two-step process as evidenced by the appearance of discrete diazenium radicals.

The similarity in the photochemical and thermal reactions of azoesters led us earlier to suggest that they proceed via a common intermediate, triplet excited azoester.⁸ This species had as yet not been observed. We therefore photolysed a series of azoesters (1a - 1c) in the cavity of an ESR spectrometer at various temperatures. No triplet species were detected, indicating that they are either unimportant in the photoreactions of azoester or too short lived to be observed even at 77 K. Instead, ESR signals were observed which appear to stem from the diazenium radicals 2a - 2c (Table 1).



The ESR spectrum of the radical formed from dimethyl azodicarboxylate (1a) is shown in Fig. 1. The hyperfine splitting pattern obviously arises from the interaction of an unpaired electron with two non-equivalent nitrogen atoms and three equivalent protons (a_N 8.56 and 1.78 G, a_H 0.38 G). The splittings are of the same magnitude as those observed for the radical anion of dimethyl azodicarboxylate (a_N 5.9 G, a_H 0.9 G).⁹

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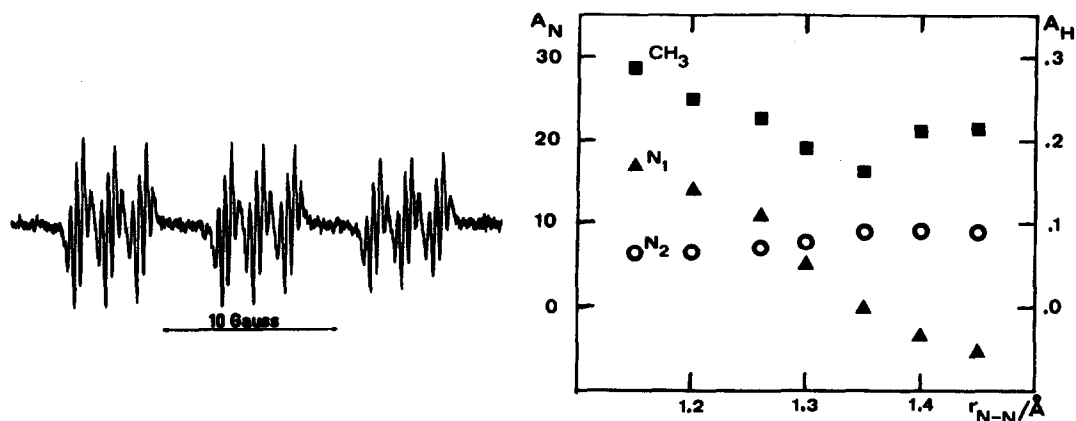


Fig. 1. ESR spectrum at 25° of the radical formed on photolysis of 1a.

Fig. 2. Calculated hyperfine coupling constants (in G) for the $\text{CH}_2\text{O}(\text{CO})\text{NN}$ radical at various N-N distances. (N_2 refers to the terminal nitrogen.)

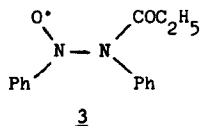
Table 1. Hyperfine coupling constants (in G) and g values of the radicals formed on photolysis of the azoesters 1a - 1c.

Ester	Dimethyl- ($+25^\circ$)	Diethyl- (-60°)	Di-t-butyl- (-60°)
a_{N}	8.56 ± 0.05	8.50 ± 0.05	8.56 ± 0.05
a_{N}	1.78 ± 0.03	1.85 ± 0.05	1.75 ± 0.05
a_{H}	0.38 ± 0.02	0.39 ± 0.02 (CH_2)	not resolved
linewidth	0.2	0.3	0.5
g value	not measured	2.0063 ± 0.0002	not measured

The diazenium radicals were unaffected by radical scavengers like oxygen, which merely caused reversible broadening of the signals, and could not be trapped by 2-methyl-2-nitrosobutanone-3.¹⁰ The unusual stability of the radicals 2a - 2c is further shown by their half lives of about 1 min at 25° .

It is difficult to explain why earlier workers have failed to observe diazenium radicals of type 2.^{7,11} One possibility is of course that we have been observing radicals which stem from some impurity. However, we could not detect any impurities in our samples by TLC.

The similarity between our observed spectra and that of compound 3 ($a_{\text{N}} = 1.67$ and 11.61 G)¹² indicates that a structure related to 3 is also possible.



It is difficult to envisage a reasonable structure of this type derived from azoester. We therefore strongly favour the diazenium structure 2 for the observed radicals.

This assignment further supported by the result of an INDO calculation of the splittings as a function of the nitrogen-nitrogen distance in a radical of the type 2 (Fig. 2).¹³ At $N-N = 1.33 \text{ \AA}$, $a_{N_1} = 1.8 \text{ G}$, $a_{N_2} = 8.8 \text{ G}$, and $a_H = 0.17 \text{ G}$, which is in good agreement with the observed values.

While isotope effects and chemical evidence indicate that unsymmetrical azo compounds may be decomposed in a stepwise manner,^{2,4,5} it has been suggested that the decomposition of symmetrical azo compounds is concerted.^{2,3} The photochemical decomposition of azoisobutyronitrile may be an exception. This reaction has been claimed to generate a diazenium radical but the claim has been disputed.⁶ However, our results show that a stepwise cleavage is indeed possible also for symmetrical azo compounds.

Experimental

ESR-Spectra were recorded with a Varian E-3 spectrometer equipped with standard quartz insert dewar and variable temperature accessory. The whole sweep range (0-6800 G at 9.2 GHz) was investigated in the attempts to observe triplets. Hyperfine splittings were determined relative to Fremy's radical (13.0 G) and g values relative to DPPH (2.0036). Degassed 0.005 M solutions in 20:80 isopentane-methylcyclohexane were used. The hydrocarbons were purified according to Murray and Keller.¹⁴

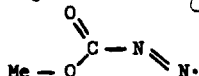
A Philips SP 900 W high pressure mercury lamp was used for the irradiations, which were generally done at -60° . Irradiations at -196° , -60° and $+25^\circ$ gave essentially the same results.

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13. The program CNINDO, written by P.A. Dobosh (QCPE 141), was kindly supplied by Dr. B. Nelander, Thermochemistry Laboratory, University of Lund. The following bond lengths were used (Å): C-H 1.10, C-O 1.36, C=O 1.23, C-N 1.32; all bond angles were taken to be 120° , in an assumed conformation:



- INDO calculations of hyperfine coupling constants have recently been discussed: M.F. Chin, B.C. Gilbert and B.T. Sutcliffe, J. Phys. Chem. **76**, 553 (1972).
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