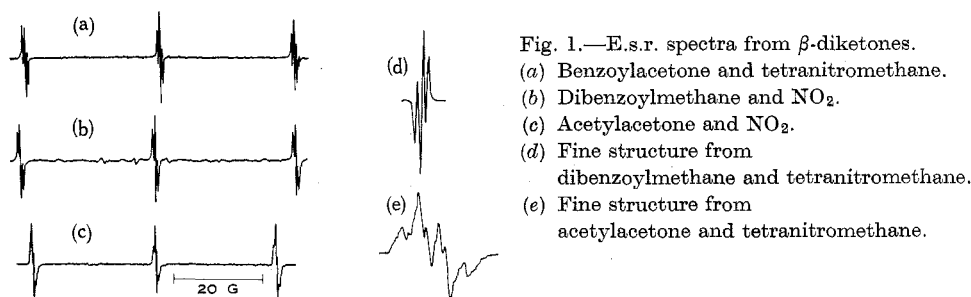


FREE RADICAL ADDUCTS OF NITROGEN DIOXIDE*

By A. HUDSON†

It has been shown that ultraviolet irradiation of a solution of tetranitromethane containing an unsaturated organic compound may lead to the formation of free radicals detectable by electron spin resonance.^{1,2} Later work established that similar species may be prepared by base decomposition of such solutions and it was suggested that the free radical formation involved the transfer of one or two nitro groups from tetranitromethane to the acceptor molecule.³ In further investigating these reactions we have shown that in many cases identical radicals are produced when nitrogen dioxide is added to a solution of the organic molecule in chloroform. This is in agreement with studies of the photo-decomposition of tetranitromethane in an inert matrix at 77°K which suggest⁴ that the primary step is $C(NO_2)_4 \rightarrow NO_2 + C(NO_2)_3$.



Typical spectra obtained from β -diketones are shown in Figure 1, and the splitting constants are given in Table 1. The spectra are better resolved than those obtained previously and the small proton hyperfine splittings of the large nitrogen triplet are characteristic of the acceptor. This behaviour is similar to that found in an investigation of charge transfer from NO_2 to a number of organic acceptors,⁵ and indicates that in these complexes approximately 50% charge transfer has occurred.

The radicals were stable in the absence of air for periods of several hours; however, a slow reaction leads to eventual oxidation of the methylene group.⁶ The

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¹ Lagercrantz, C., and Yhland, M., *Acta chem. scand.*, 1962, **16**, 1807.

² Lagercrantz, C., Preprints 6th Int. Symp. Free Radicals, Cambridge 1963.

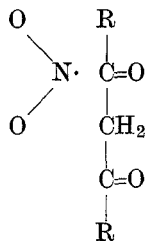
³ Lagercrantz, C., *Acta chem. scand.*, 1964, **18**, 383.

⁴ Bielski, B. H. J., and Timmons, R. B., *J. phys. Chem.*, 1964, **68**, 347.

⁵ Schaafsma, T. J., and Kommandeur, J., *J. chem. Phys.*, 1965, **42**, 438.

⁶ Wieland, H., and Bloch, S., *Ber. dt. chem. Ges.*, 1904, **37**, 1524.

structure of the observed species is open to speculation since a charge-transfer complex between NO_2 and the enol of the diketone does not readily explain the interaction with two equivalent protons. The configuration



is in agreement with the e.s.r. data, but further evidence is required before any firm assignment can be made.

TABLE I
HYPERFINE COUPLING CONSTANTS (in G) FOR RADICALS FROM
 β -DIKETONES

Diketone	A_N	$2A_H^*$	$3A_H^\dagger$
$\text{CH}_3\text{COCH}_2\text{COCH}_3$	27.63	0.30	0.45
$\text{PhCOCH}_2\text{COPh}$	30.40	0.60	—
$\text{PhCOCH}_2\text{COCH}_3^\ddagger$	30.40	0.60	—

* 1 : 2 : 1 triplet from two equivalent protons.

† 1 : 3 : 3 : 1 quartet from three equivalent protons.

‡ The spectrum is slightly asymmetric, suggesting the presence of a second species.

A number of other systems have been examined and, although in many cases free radicals have been observed, the species formed from tetranitromethane is not always identical with that formed by addition of NO_2 . Cyclohexene gives three lines of equal intensity split by 12.4 G on addition of NO_2 whereas irradiation of the tetranitromethane adduct gives a 1 : 2 : 3 : 2 : 1 quintet of triplets.¹