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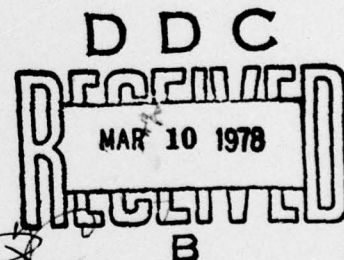
MEMORANDUM REPORT ARBRL-MR-2799

ELECTRON SPIN RESONANCE OF THE RADICAL
COMPLEXES $(\text{NO}_2)_2$, $(t\text{-BuO})_2$, AND $(\text{CH}_3)_2$
IN AN ARGON MATRIX AT 10K

Cornelius U. Morgan

November 1977

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USA ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) ssv/4589 In the present electron spin resonance (esr) study nitrate esters or t-butyl peroxide in an inert gas (1:100) are pyrolyzed to produce the mono- radicals NO ₂ , CH ₃ , and t-BuO. The pyrolysis products and inert gas are collected as a solid at 10K. In the solid phase some of the monoradicals associate to form the radical complexes (NO ₂) ₂ , (CH ₃) ₂ , and (t-BuO) ₂ . The in- tegrated intensity of the complex in these cases is always about four orders of magnitude less than the integrated intensity of the monoradical. This fact →		

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tends to support the possibility that the complex will be formed from any monoradical that reaches a certain threshold concentration.

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The electron spin resonance (esr) of a triplet state produced by the association of a H atom and methyl radical was first observed by Gordy and Morehouse¹ in solid methane at 4.2K. Trozzolo, Murray, Smolinsky, Yager, and Wasserman^{2,3} have observed the esr of the ground state triplets of a number of methylenes and nitrenes. The triplet character of the esr spectra of the nitroxide biradicals, tetramethyl-2,2,6,6, piperidinol-4 glutarate and tetramethyl-2,2,6,6, piperidinol-4 terephthalate, was demonstrated by Falle et al⁴ in liquid crystal solutions.

While making an esr study of the products of the pyrolysis of gaseous nitrate esters a " $\Delta m = 2$ " transition was observed at the half field position of 166.21 mT and klystron frequency $\nu = 9316$ MHz (Figure 1A). In these experiments the nitrate ester in argon (1:100) stored in a one liter reservoir at 760 torr was passed from the reservoir through a precision leak valve for one hour at the rate of 3.6×10^{-6} m³/minute through a cylindrical quartz furnace heated by a coil of nichrome wire into an evacuated cryogenic refrigerator where the pyrolysis products were condensed to a solid on a sapphire rod cooled to 10K. The cryotip of the refrigerator which enclosed the cooled sapphire rod was then placed in the esr cavity and the spectra observed. In these runs whenever the " $\Delta m = 2$ " transition was observed the concentration of the NO₂ radical at $g = 2$ was about 10^{25} spins/m³. Because of the extremely high concentration of NO₂ in these runs it was suspected that the spectrum observed at half field was an associative complex of NO₂.

To test this theory one sample of NO₂ in argon (1:50) was passed through the furnace at a temperature of 620 K for 30 minutes and another (1:30) was run at ambient temperature for the same period and the products collected on the sapphire rod in each case. The same esr spectrum of five lines with intensity distribution of 1:2:3:2:1 and hyperfine splitting constant of 2.77 mT was observed in these two cases as with the nitrate esters (Figure 1A). From the results of these runs it was concluded that the spectrum was produced by the interaction of two equivalent nitrogen atoms contained in a radical complex such as (NO₂)₂ with the free electrons. This spectrum did not decrease in intensity after several hours of monitoring at 10 K. In these two NO₂ runs, the concentration of NO₂ observed was 10^{26} spins/m³. The integrated intensity of the spectrum of the NO₂ radical in these two cases was about four orders of magnitude higher than the integrated intensity of the (NO₂)₂ spectrum.

¹ W. Gordy and R. Morehouse, *Phys. Rev.* **151**, 207 (1966).

² A. M. Trozzolo, R. W. Murray, G. Smolinsky, W. A. Yager, and E. Wasserman, *J. Am. Chem. Soc.*, **85**, 2526 (1963).

³ E. Wasserman, G. Smolinsky, and W. A. Yager, *J. Am. Chem. Soc.*, **86**, 3166 (1964).

⁴ H. R. Falle, G. R. Luckhurst, H. Lemaire, Y. Marechal, A. Rassat, and P. Rey, *Mol. Phys.* **11**, 49 (1966).

In some similar thermal decomposition work on t-butyl peroxide in argon, two different " $\Delta m = 2$ " transition spectra were observed. When t-butyl peroxide in argon (1:100) was pyrolyzed at 730 K, a single line spectrum due to a " $\Delta m = 2$ " transition was observed (Figure 1B). This spectrum observed at a field of 164.43 mT was produced by the complex $(t\text{-BuO})_2$. The concentration of t-BuO radical at $g = 2$ was 10^{25} spins/ m^3 . The integrated intensity of the t-BuO radical spectrum in this run was four orders of magnitude higher than the integrated intensity of the spectrum of the $(t\text{-BuO})_2$ complex.

When a mixture of t-butyl peroxide in argon (1:100) was heated at 600 K, two " $\Delta m = 2$ " spectral transitions were observed (Figure 1C). The most intense of these appeared at a field of 166.17 mT. The spectrum consisted of seven lines with an intensity distribution of 1:6:15:20:15:6:1 and hyperfine splitting constant of 1.14 mT. This spectrum was produced by the $(\text{CH}_3)_2$ complex by the interaction of six equivalent protons with the free electrons. This spectrum is displaced about the base line due to the presence of the single line spectrum of $(t\text{-BuO})_2$. The concentration of methyl radicals at $g = 2$ in this run is 10^{25} spins/ m^3 . The concentration of the t-BuO radical in this instance is masked by the high concentration of the methyl radical. Complexes $(\text{CH}_3)_2$ and $(t\text{-BuO})_2$ are stable at 10 K and no change in concentration is noticed after an hour of monitoring. The integrated intensity of the methyl radical spectrum in this run was four orders of magnitude higher than the integrated intensity of the spectrum of the $(\text{CH}_3)_2$ complex.

Since these radical complexes have been observed in each of the few cases that have been examined, the possibility exists that when the concentration of any radical reaches a certain threshold value, the " $\Delta m = 2$ " transition complex should be observed.

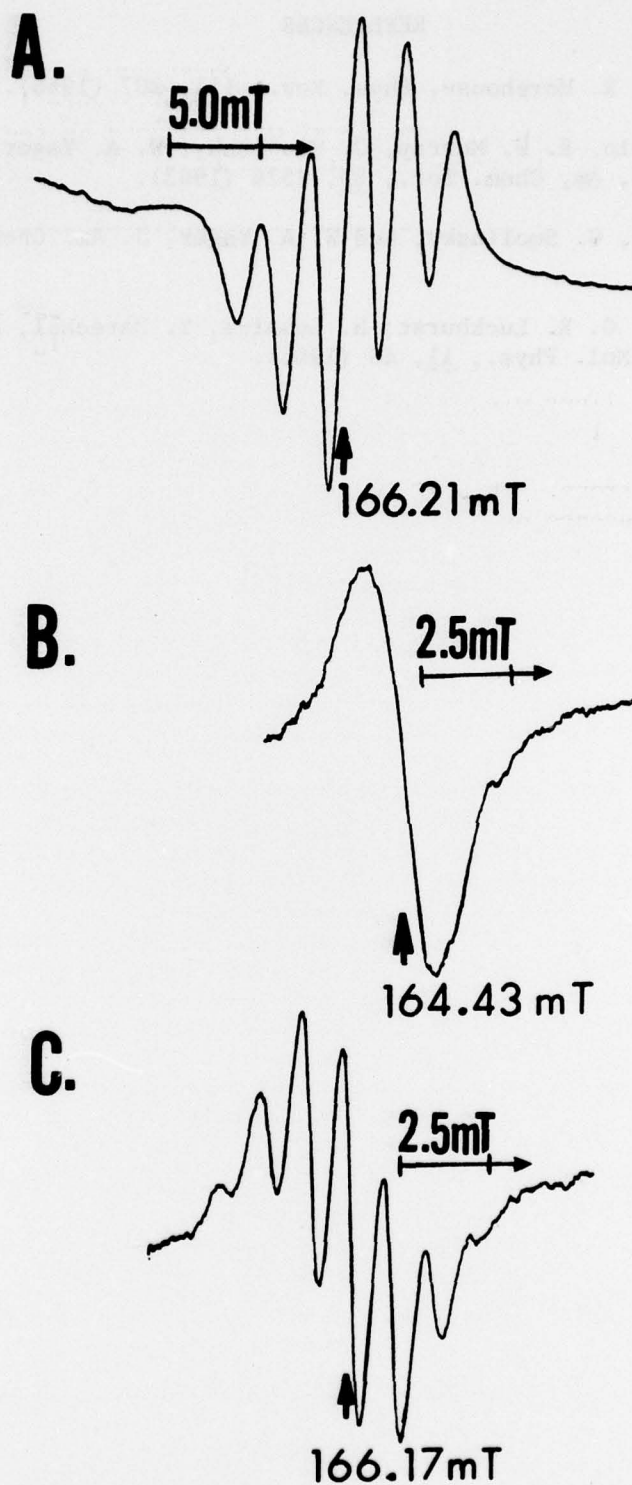


Figure 1. Spectra of Radical Complexes: A. $(\text{NO}_2)_2$; B. $(\text{t-BuO})_2$; and C. $(\text{CH}_3)_2$ and $(\text{t-BuO})_2$

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3. E. Wasserman, G. Smolinsky, and W. A. Yager, J. Am. Chem. Soc., 86, 3166 (1964).
4. H. R. Falle, G. R. Luckhurst, H. Lemaire, Y. Marechal, A. Rassat, and P. Rey, Mol. Phys., 11, 49 (1966).

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