Electron Spin Resonance Study of Carbamoyl Radical*[1]

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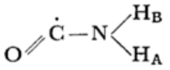
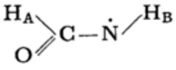
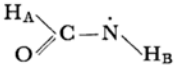
An ESR study is made of intermediate radicals in the oxidation of amides with hydroxyl radical in aqueous solution by using rapid flow technique with hydrogen peroxide and titanous chloride redox system. The ESR spectrum attributed to acyl type radical is observed. The ESR parameters of the radical from formamide are $g=2.00167$, $a_N=21.8$ gauss (one nitrogen nucleus), $a_H=30.8$ gauss (one proton), and $a_H=1.3$ gauss (one proton). Smith and Wood[1)] observed the same spectrum and assigned the radical to $HCO\dot{N}H$ (π electron radical). But we identify it as $NH_2\dot{C}O$ (carbamoyl σ electron radical) according to the following consideration.

One of characteristics of the spectrum is that the g value is smaller than that of free spin (2.00232). Unusually small g values are observed for some σ electron radicals such as vinyl (2.00220)[2a)] and formyl (2.0009)[2b)] radicals, on the other hand g value of the π electron radical is generally larger than 2.00232.[3)] So the radical from formamide is considered to be a σ electron radical with a configuration I, II, or III.


I


II


III

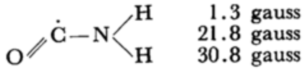
Isotropic hyperfine coupling (hfc) constants and g values of the radicals with structures I, II, and III are calculated with the extended Hückel method.[4,5)] The calculated g value[3)] for I is 2.00131, for II 2.00427, and for III 2.00984. In Table 1 the calculated hfc constants[4b)] are compared with the observed ones.

TABLE 1. CALCULATED hfc CONSTANTS

	a(N)	a(H_A)	a(H_B)
(I)	8.0	31.3	3.1
(II)	1.9	115.9	4.3
(III)	30.2	92.0	33.5
Observed	21.8	30.8	1.3

Only the calculated g value for I is smaller than the g value of free spin (2.00232), and shows a good agreement with the observed value. The calculated hfc constants for I also agree with the observed ones. In view of the above bases it can be concluded that the observed radical is carbamoyl σ electron radical.

These calculated results suggest that in the carbamoyl radical the larger one of the hfc constants of the two protons is due to the *trans* proton to the odd electron orbital and the smaller one to the *cis* proton.



This assignment is consistent with those of vinyl[2a)] and iminoxy[6)] radicals.

N-Alkyl substituted carbamoyl radicals as well as other π electron radicals formed in the oxidation of amides will be reported in near future.

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*[1] Presented at the Sixth Symposium on ESR, Kyoto, Oct., 1967.

1) P. Smith and P. B. Wood, *Can. J. Chem.*, **44**, 3085 (1966).

2) a) E. L. Cochran, F. J. Adrian and V. A. Bowers, *J. Chem. Phys.*, **40**, 213 (1964); b) F. J. Adrian, E. L. Cochran and V. A. Bowers, *ibid.*, **36**, 1661 (1962).

3) A. J. Stone, *Mol. Phys.*, **6**, 509 (1963).

4) a) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179, 3489 (1962); b) G. A. Petersson and A. D. McLachlan, *ibid.*, **45**, 628 (1966).

5) In the extended Hückel calculation, the orbital exponent of the Slater type atomic orbital for hydrogen is set equal to 1.2. The calculated results show that in all the structures the odd electron occupies a σ orbital.

6) W. M. Fox and M. C. R. Symons, *J. Chem. Soc., (A)*, **1966**, 1503.