BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(6), 1541—1542 (1974)

The ESR Spectra of Michler's Ketone Anion Radicals

Hideo FUJITA, Saburo KAKO, Jun YAMAUCHI*, Hiroaki OHYA-NISHIGUCHI**, and Yasuo DEGUCHI
College of Liberal Arts and Sciences, Kyoto University, Kyoto 606
* *Institute for Chemical Research, Kyoto University, Uji 611*
** *Faculty of Science, Kyoto University, Kyoto 606*

(Received November 12, 1973)

Synopsis. The ESR spectra of Michler's ketone anion radicals reduced by alkali metal in solution consist of five groups of lines at +20 °C, but change into three groups of lines at −50 °C. The assigned hyperfine splitting constants are $A_{\mathrm{H}}^{o}=3.22$, $A_{\mathrm{H}}^{m}=0.43$, $A_{\mathrm{N}}=0.72$, $A_{\mathrm{H}}^{\mathrm{CH_3}}=0.29$ gauss at +20 °C.

Since Müller[1)] reported the complete 1 : 1 metal ketyl monomer fomation of Michler's ketone with counter cations on the basis of magnetic-susceptibility measurements, the cation radicals of this ketone[2)] in solution have been investigated by ESR and characterized as similar to those of Wuerster's blue[3)] and *N,N'*-tetramethylbenzidine[4)] in the relative magnitudes of their hyperfine splitting constants among nitrogen and differrent sorts of protons. The results of the first observation of the ESR spectra of anion radicals of this ketone will be presented in this report.

Experimental

Anion radicals of Michler's ketone were prepared by the standard alkali metal reduction method.[5)] The ESR spectra were measured with a JEOL X-band spectrometer equipped with 100 kHz modulation (MODEL ME-3) over the temperature range from +90 to −120 °C. Spectral simulations were carried out with a JEOL Spectral Computer (MODEL JEC-6).

Results and Discussion

The ESR spectra of the anion radicals obtained by potassium metal reduction on a mixed solvent (75%-DME and 25%-MeTHF) consisted of five groups of lines in the temperature range from 0 to +40 °C; a typical example at +20 °C is shown in Fig. 1a. Upon cooling to a lower temperature range (from −30 to −60 °C), the spectral structures were changed into those of three groups of lines with an approximate intensity ratio of 1 : 2 : 1; a representative spectrum at −50 °C is shown in Fig. 2. No appreciable line broadening has been detected in this temperature region, and the overall spectral width was constant at a value of around 21.2 gauss. The temperature dependency was found to be reproducible even when the temperature was changed to the reverse. The slightly broader linewidth on the high-field side than on the low-field side seems to be attributable to the contribution from the anisotropic *g*-tensor.[6)]

A satisfactory simulation spectrum for Fig. 1a is shown in Fig. 1b, while the splitting constants used are compiled in Table 1 together with the corresponding spin densities calculated by H.M.O. procedures (using the hyperconjugation model[7)] for the methyl-group

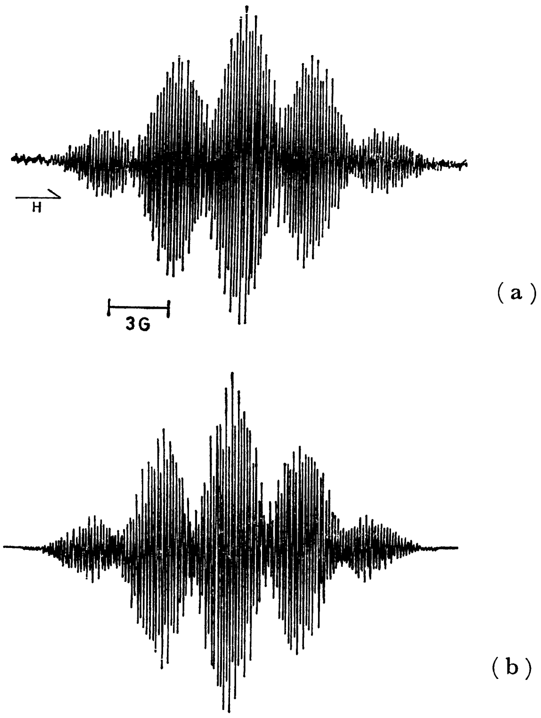
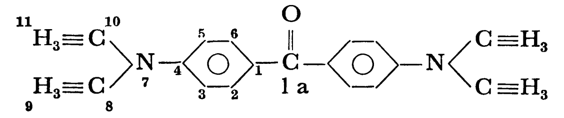


Fig. 1. The ESR spectrum of Michler's ketone anion radical in mixture of DME(75%) and MeTHF(25%) at +20 °C. The upper spectrum (a) is the experimental and the lower (b) is the simulation based on the splitting constants given in Table 1.

TABLE 1. SPIN DENSITIES AND SPLITTING CONSTANTS AT +20 °C FOR MICHLER'S KETONE ANION RADICAL

Positions	Calcd Spin Densities[a)] Hückel	Calcd Spin Densities[a)] McLachlan	Calcd h. f. s. Const.[b)] (gauss)	Obsd h. f. s. Const (gauss)
1 a	0.3012	0.4054		
1 b	0.1061	0.1204		
1	0.0051	−0.0466		
2, 6	0.0829	0.1110	2.66	3.22
3, 5	0.0012	−0.0379	0.91	0.43
4	0.0753	0.0889		
7	0.0409	0.0432	0.86	0.72
8, 10	0.0000	−0.0012		
9, 11	0.0031	0.0034	0.57	0.29

a) The parameters used for the calculation were cited from Ref. 7.



b) These values were calculated by using McLachlan spin densities in the table with Q values: $|Q_{\mathrm{C\text{-}H}}^{\mathrm{H}}|=24$, $|Q_{\mathrm{C\text{-}N}}^{\mathrm{N}}|=20$, $|Q_{\mathrm{CH_3}}^{\mathrm{H}}|=508/3$

contributions). The 3.22 gauss splitting from *o*-proton frames the characteristic five-group structure. The structure in the groups is accounted for by the contribution of the nitrogen and the other proton splittings. The potassium metal splitting constant is estimated to be less than 0.08 gauss; thus, the spectral patterns have not been affected significantly.

The change in the spectral structures around −30 °C to −60 °C has not yet been explained satisfactorily. However, the present authors assume that either a non-equivalency in a pair of *o*- or *m*-protons on the respective phenyl rings in the molecule or the presence of a linewidth alternation[8] similar to those found in the case of benzophenone[9] is responsible for this peculiar change. Many simulations for Fig. 2 have been carried out following a couple of the aforementioned mechanisms, but no statisfactory agreements have yet been found.

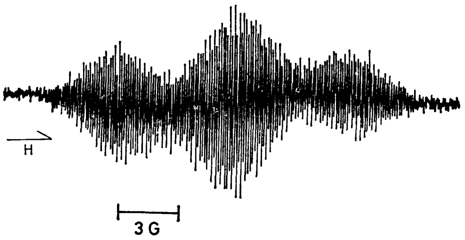


Fig. 2. The ESR spectrum of Michler's ketone anion radical in mixture of DME(75%) and MeTHF (25%) at −50 °C.

Recently the triplet-state ESR spectra of Michler's ketone ketyl have been observed; they suggest the formation of a metal ketyl similar to that of benzophenone.[10] These results will be reported in detail elsewhere.

References

1) E. Müller und W. Janke, *Z. Elektrochem.*, **45**, 380 (1939).
2) B. M. Latta and R. W. Taft, *J. Amer. Chem. Soc.*, **89**, 5172 (1967).
3) J. R. Bolton, A. Carrington, and J. D. Santos-Veiga, *Mol. Phys.*, **5**, 615 (1962).
4) J. M. Fritsch and R. N. Adams, *J. Chem. Phys.*, **43**, 1887 (1965).
5) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Amer. Chem. Soc.*, **78**, 116 (1956). H. Nishiguchi, Y. Nakai, K. Nakamura, K. Ishizu, Y. Deguchi, and H. Takaki, *J. Chem. Phys.*, **40**, 241 (1964).
6) R. D. Allendoerfer, *J. Magn. Resonance*, **9**, 140 (1973).
7) Y. Ikegami, H. Watanabe, and S. Seto, This Bulletin, **45**, 2205 (1972). A Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, New York (1962), p. 135.
8) P. D. Sullivan and J. R. Bolton, "Advances in Magnetic Resonance," ed. by J. S. Waugh, Vol. 4, Academic Press, New York and London, (1970), p. 39.
9) T. Takeshita and N. Hirota, *J. Chem. Phys.*, **51**, 2146 (1969).
10) N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, **86**, 2538 (1964). N. Hirota, *ibid.*, **89**, 32 (1967).