Chemical Shifts of the Proton Magnetic Resonance in Alkylhydroperoxides[*]

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Chemical shifts of the proton magnetic resonance in alkylhydroperoxides were measured in order to obtain the NMR informations of these compounds which have not been reported. The samples are listed in Table I with their characteristic data. All of them except *tert*-butylhydroperoxide were synthesized by one of us (S. K.) according to the methods reported by Williams and Mosher[1]. The *tert*-butylhydroperoxide was obtained commercially from the International Chemical Company.

TABLE I. SAMPLES OF NMR MEASUREMENTS

n-Propyl hydroperoxide	35°C/20 mm.	$n_D^{25}=1.3890$
n-Butyl hydroperoxide	28∼29°C/5 mm.	$n_D^{20}=1.4057$
sec-Butyl hydroperoxide	41∼42°C/11 mm.	$n_D^{20}=1.4050$
n-Amyl hydroperoxide	41∼42°C/4 mm.	$n_D^{20}=1.4146$
n-Octyl hydroperoxide	64∼66°C/0.7 mm.	$n_D^{20}=1.4311$

tert-Butylhydroperoxide was obtained commercially.

The apparatus used for the measurements of the chemical shifts is the one constructed in this laboratory using the permanent magnet manufactured by the Indiana Steel Company and the resonant frequency is about 27.030 Mc. ($H_0=6300$ gauss). The chemical shift of the OOH proton resonance in each compound was measured as the separation from CH_3 signal appearing as the peak in the highest field on the recorded charts taking the cyclohexane and benzene mixture (0.28 g. +0.30 g.) as the reference to show the separation of 227 cps. at 40 Mc.

According to the results of the measurements, the resonant positions for the OOH protons are in the field lower than those for CH_3 by about 245 (±5) cps., being close to the value for COOH proton in aliphatic acid, 267 (±3) cps. for *n*-butylric acid, or about 280∼230 cps.[2], and less shielded than the OH protons in alcohols which were measured as 120 (±5) cps. or 120∼100 cps[2]. The propylhydroperoxide showed a very small value of 222 (±5) cps., and this was assumed to be due to the decomposition of the compound. The figures showing the variations of the observed data are due to the overlapping and the incomplete separation of the signals of CH_3 and CH_2's.

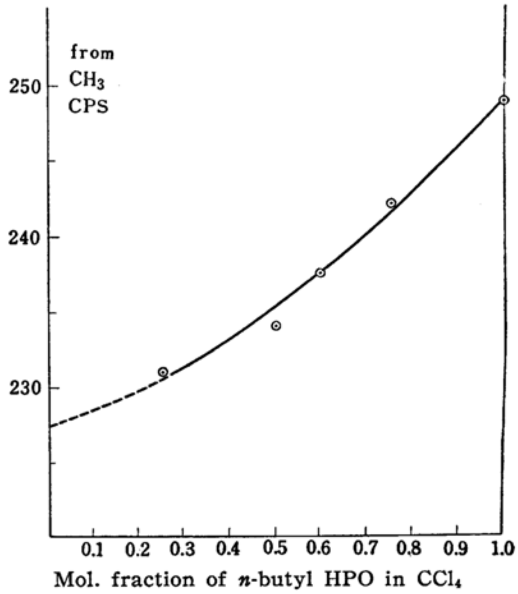

Fig. 1

In order to investigate the effects of the decomposition of the samples, the concentration dependence of the shifts were measured for the carbon tetrachloride solutions of the *n*-butylhydroperoxide.

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[1] H. R. Williams and H. S. Mosher, *J. Am. Chem. Soc.*, 76, 2984 (1954).

[2] These values were obtained from Fig. 6 in the article given by N. F. Chamberlain, *Anal. Chem.*, **31**, 56 (1959).

The results are as shown in Fig. 1, it is seen that the OOH signal is shifted to the lower field with the increase of the concentration of the hydroperoxide, and this result will be interpreted in terms of the destruction of the structures of associated molecules as in the cases of other hydrogen-bonded liquids[3,4]. The susceptibility corrections are not made in the results of Fig. 1. Since the concentration dependence is so large that the results of the measurements with one another shifts are to be compared to each other at the same conditions of concentration. As the hydroperoxides are unstable and, moreover, it is rather difficult to determine their concentrations, we made the measurements immediately after the preparation of the samples. Hence, the results of Fig. 1 are assumed to refer to those for the actually pure hydroperoxides which are not so much different from one another in the concentration. It is also noted that α-CH_2 protons in all the samples fall in almost same position of about 79 (±1) cps. away from CH_3. Since the α-CH_2 protons in alcohols with the same carbon number as the samples showed the value of 65 (±2) cps., we notice that α-CH_2 protons in hydroperoxides are less shielded than those in alcohols as well as OOH protons. In comparison with aliphatic acids, the COOH protons which are expected to be away from CH_3 by about 275~230 cps.[2] are, as noted above, very close to the OOH protons in hydroperoxides, while α-CH_2 protons in acids are only 35 cps.[2] away from CH_3 and more shielded than those in hydroperoxides and in alcohols. Therefore, it is a quite interesting problem to investigate the chemical characters of alcohols, hydroperoxides and acids from the viewpoint of structures and of electronic distributions of OH, OOH and COOH groups.

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[3] J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

[4] L. W. Leeves and W. G. Schneider, *Trans. Faraday Soc.*, **54**, 314 (1958).