NMR Spectra of Formals, Acetals and the Related Compounds

By Kenkichi NUKADA and Utako MAEDA

(Received April 22, 1959)

It is interesting to study the NMR spectra of formals (R_1-O-CH_2-O-R_2), acetals (R_1-O-CH(CH_3)-R_2) and the related compounds (H-C(OR)$_3$ and R-(O-CH_2-CH_2)$_n$-OR), as these compounds contain functional groups such as CH_3-O, CH_3-CH_2-O, O-CH_2-CH_2-O, O-CH_2-O, H-C(O)(O)-CH_3, etc. It is quite difficult, or sometimes perfectly impossible, to identify some of these functional groups by the infrared spectroscopy[1]. We have tried to identify them by the high resolution NMR spectroscopy[2]. JNM-3 (Japan Electron Optics Laboratory Co.) and 4300-B (Varian Associates) spectrometers were used.

Fig. 1 shows the NMR spectra of benzene solutions of several compounds except dimethyl acetal (CH_3-O-CH(CH_3)-O-CH_3), acetal (C_2H_5-O-CH(CH_3)-O-C_2H_5) and diethylene-glycol diethyl ether (C_2H_5-(O-CH_2-CH_2)$_2$-O-C_2H_5). The spectra of these three compounds were obtained in pure liquid phase and reference bands are shown with arrows on the peaks of each spectrum. The unit of abscissa means the chemical shift from the signal of benzene protons. The tentative assignments are shown on the tops of each peak.

TABLE I. THE VALUES OF CHEMICAL SHIFTS OF FUNCTIONAL GROUPS

Type of group	Chemical shift from benzene protons ($\times 10^{-7}$)
H-C(O)(O)(O)	21.3
(H)-C(O)(O)-CH_3	27.5
O-CH_2-O	27.8±1.0
O-CH_2-C	37.8±2.0
CH_3-O	40.3±0.8
(CH_3)-C(O)(O)-H	62±2
(CH_3)-CH_2-O	61±3

1) K. Nukada, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), in press.

2) Chamberlain reported the NMR spectra of several hundreds of compounds including some ethers and alcohols, but in his paper those of above-mentioned compounds have not been reported. (N. F. Chamberlain, *Anal. Chem.*, 31, 56 (1959)).

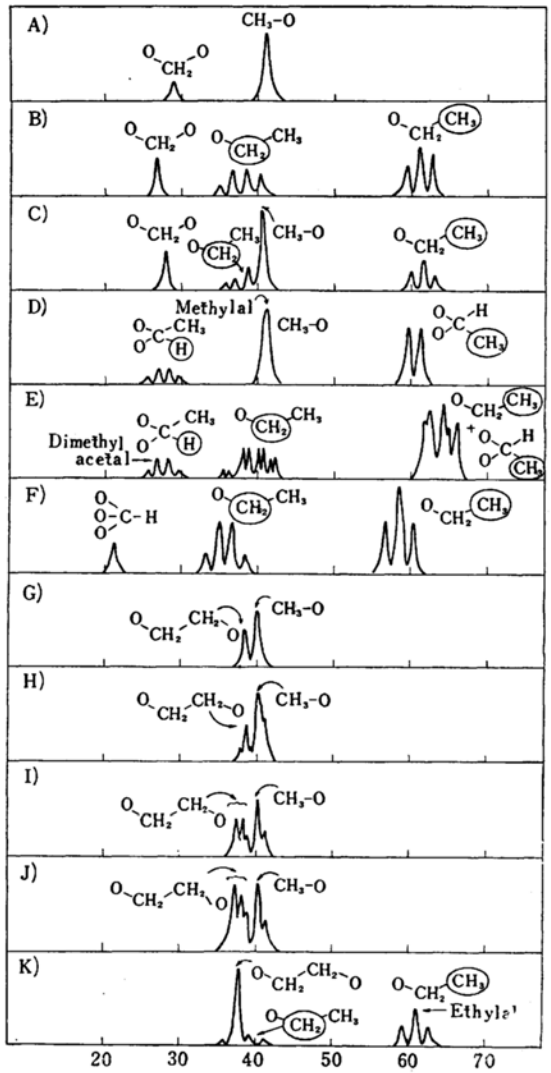

Fig. 1. Proton magnetic resonance spectra of formals, acetals and the related compounds.

A. Methylal. ($CH_3OCH_2OCH_3$)
B. Ethylal. ($CH_3CH_2OCH_2OCH_2CH_3$)
C. Methyl-ethyl formal. ($CH_3CH_2OCH_2OCH_3$)
D. Dimethyl acetal. ($CH_3OCH(CH_3)OCH_3$)
E. Acetal. ($CH_3CH_2OCH(CH_3)OCH_2CH_3$)
F. Orthoformic acid ethyl ester. ($CH(OCH_2CH_3)_3$)
G. Ethylene glycol dimethyl ether. ($CH_3OCH_2CH_2OCH_3$)
H. Diethylene glycol dimethyl ether. ($CH_3(OCH_2CH_2)_2OCH_3$)
I. Triethylene glycol dimethyl ether. ($CH_3(OCH_2CH_2)_3OCH_3$)
J. Tetraethylene glycol dimethyl ether. ($CH_3(OCH_2CH_2)_4OCH_3$)
K. Diethylene glycol diethyl ether. ($CH_3CH_2(OCH_2CH_2)_2OCH_2CH_3$)

We wish to express our sincere thanks to Dr. Y. Mashiko of this Institute, Dr. S. Hattori of Kanazawa University and Dr. T. Seki of Japan Electron Optics Laboratory Co. for their kind advice and to Dr. H. Honda and Dr. K. Nagata of the Resources Research Institute who kindly measured a part of spectra.

Government Chemical Industrial Research Institute of Tokyo
Hatagaya Honmachi,
Shibuya-ku, Tokyo