BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (10), 2819—2820 (1977)

The Effects of Solvents on the Electronic Absorption Spectrum of Sodium 4-Nitrophenoxide in the Presence of 15-Crown-5 Ether

Shinichi Ueji and Masayuki Kitadani
Institute of Chemistry, College of General Education, Kobe University, Tsurukabuto, Nada, Kobe 657

(Received April 14, 1977)

Synopsis. The electronic absorption spectrum of sodium 4-nitrophenoxide was determined in 21 solvents of varying polarities by the aid of the ability of 15-crown-5 ether to solubilize the salt in nonpolar solvents. These spectra showed a marked difference between hydroxylic solvents and nonhydroxylic solvents. A possible interpretation for this difference is presented.

In the course of our study of the relationships between solvent polarity parameters and solvent-induced spectral shifts in spectroscopic investigations, we previously observed interesting solvent effects on the IR frequency shifts[1)] and on the NMR chemical shifts.[2)] In this report the effects of solvents on the electronic absorption spectrum of sodium 4-nitrophenoxide will be discussed on the basis of the correlation between the solvent shifts and Dimroth's solvent polarity parameter, E_t (hereafter abbreviated as D's E_t), values.[3)]

Results and Discussion

The Table summarizes the solvent-induced spectral shifts for sodium 4-nitrophenoxide relative to 4-nitroanisole in a range of solvents. In certain nonpolar solvents, in order to obtain a solubility of the salt sufficient for the measurement of the λ_{max} value, a large excess of the sodium chelatent, 15-crown-5 ether, was used. Since it is desirable that solvent shifts be compared under the same conditions, all the spectra were measured in the presence of a large excess of the crown ether. The crown ether's effects on the spectra are also given in the Table.

It is found that the enhanced red shifts ($-\Delta\nu_{max}$ values in the Table) are correlated well by the D's E_t values (see Figure). As can be seen in the Figure, however, the correlation is separated into two set of straight lines, one for hydroxylic solvents and the other for nonhydroxylic solvents. Furthermore, it should be noted that the slopes of the two straight lines show opposite signs.

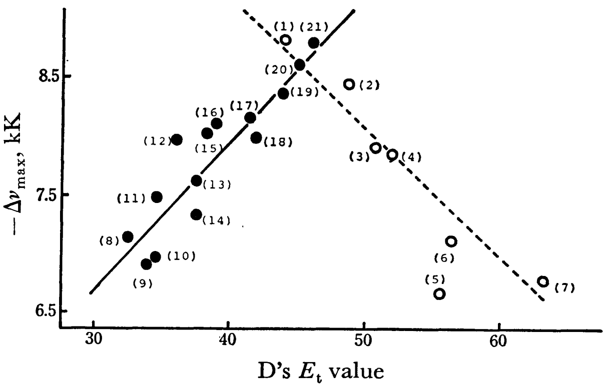

Figure. Correlation between $-\Delta\nu_{max}$ value and D's E_t value.
(○): Hydroxylic solvents, (●): nonhydroxylic solvents.

TABLE ELECTRONIC SPECTRAL SHIFTS FOR SODIUM 4-NITROPHENOXIDE (I) RELATIVE TO 4-NITROANISOLE (II) IN THE PRESENCE OF 15-CROWN-5 ETHER IN A RANGE OF SOLVENTS$^{a)}$

Solvents	λ_{max} nm (I)$^{b)}$	λ_{max} nm (II)	$-\Delta\nu_{max}$ kK$^{c)}$	D's E_t value
(1) *t*-Butyl alcohol	421.0(+1)	307.0	8.82	43.9
(2) Isopropyl alcohol	414.5(0)	307.0	8.44	48.6
(3) *n*-Propyl alcohol	407.0(0)	308.0	7.90	50.7
(4) Ethanol	406.0(0)	308.0	7.84	51.9
(5) Methanol	389.0(0)	309.0	6.65	55.5
(6) Ethylene glycol	407.5(0)	316.0	7.11	56.3
(7) Water	403.5	317.0	6.77	63.1
(8) CCl_4	385.0$^{d)}$	302.0	7.14	32.5
(9) Toluene	391.0$^{d)}$	308.0	6.89	33.9
(10) Benzene	393.0$^{d)}$	308.5	6.96	34.5
(11) Diethyl ether	391.0$^{d)}$	302.5	7.48	34.6
(12) Dioxane	407.5(+1)	307.5	7.98	36.0
(13) THF	404.0$^{d)}$	309.0	7.61	37.4
(14) Bromobenzene	406.0$^{d)}$	313.0	7.32	37.5
(15) 1,2-Dimethoxyethane	410.0(+3)	308.5	8.02	38.2
(16) $CHCl_3$	417.5$^{d)}$	312.0	8.10	39.1
(17) Dichloromethane	420.0$^{d)}$	313.0	8.14	41.4
(18) Dichloroethane	416.0$^{d)}$	312.5	7.98	41.9
(19) DMF	435.5(0)	319.0	8.36	43.8
(20) DMSO	438.0(0)	318.0	8.62	45.0
(21) Acetonitrile	429.0(0)	311.5	8.79	46.0

a) The apporopriate compound (II) was used as a reference standard, because the solvation effects on 4-nitrophenyl portion are assumed to be similar in both compounds; reproducibility <1 nm. b) The λ_{max} value is attributed to a $\pi \rightarrow \pi^*$ transition with the character of an intramolecular charge transfer from the oxygen anion to the hydrocarbon portion. The values in parentheses represent the magnitude of the crown ether effect on the λ_{max} value; positive numbers indicate red shifts. c) Enhanced red shifts for Compound (I) as compared with Compound (II);

$$-\Delta\nu_{max}, \text{kK} = [1/\lambda\ (\text{I}) - 1/\lambda\ (\text{II})] \times 10^4$$

d) Not sufficiently soluble in the absence of 15-crown-5 ether.

In the hydroxylic solvents, the phenoxide anion is presumably present as a cation-free anion rather than as sufficiently tight ion aggregates, because the anion is supposed to be strongly solvated by hydrogen bonding. Indeed, the addition of crown ether produces essentially no effect on the λ_{max} value (see Table). Therefore, it seems reasonable to assume that the hydroxylic solvent-induced shifts are mainly due to the direct H-bonding solvation of the phenoxide anion. A stronger H-bonding solvation should produce a larger blue shift, because the oxygen of phenoxide is more negative in the ground state than in the excited state. In fact, the decreasing order of the $-\Delta\nu_{\max}$ values is consistent with the α-scale of solvent H-bond donor acidities (HBD)[4] reported by Taft and Kamlet, except for the case of methanol. Furthermore, the parallelism between the $-\Delta\nu_{\max}$ value and the D's E_t value (see Figure) suggests the operation of similar H-bonding solvation mechanisms, because the D's E_t value is based on the electronic transition of the pyridinium betain with the phenoxide anion site.

On the other hand, the nonhydroxylic solvents are presumed to be poor anion solvators, so that direct solvations of the phenoxide anion can be neglected. The nonhydroxylic solvent shifts can be interpreted by assuming an interaction between the sodium cation bound by the crown ether and the phenoxide anion. It is known[5] that the D's E_t value is correlated with such measures of the ionizing power of solvents as Winstein's Y value[6] and Kosower's Z value.[7] Therefore, the increasing D's E_t value may be expected to cause a larger charge separation between the sodium cation bound by the crown ether and the phenoxide anion, and this charge separation should produce red shifts.[8] Indeed, the observed red shifts are found to be proportional to the D's E_t value (see Figure). Furthermore, the absence of any effect of crown ether in the dipolar aprotic solvents suggests that the salt is a relatively free ion.

Consequently, the $-\Delta\nu_{\max}$ value -D's E_t value correlation revealed a difference in the solvation mechanism of sodium 4-nitrophenoxide between the hydroxylic solvents and the nonhydroxylic solvents.[9]

Experimental

The electronic spectra were obtained using a Hitachi 124 automatic recording spectrophotometer. A quartz cell 1.0 cm in length was employed, and the concentration of the sample was of the order of 10^{-4} M.

Sodium 4-nitrophenoxide was prepared by a known method and dried *in vacuo* at 110 °C overnight. The solvents were freshly distilled before use, and the spectro-grade solvents were used without further purification, except for chloroform, which was chromatographed on alumina. The 15-crown-5-ether was a commercial sample (Aldrich Chemical Company, Inc.).

References

1) S. Ueji and T. Kinugasa, *Tetrahedron Lett.*, **1976**, 2037.

2) S. Ueji and M. Nakamura, *Tetrahedron Lett.*, **1976**, 2549.

3) K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Ann.*, **661**, 1 (1963).

4) R. W. Taft and M. J. Kamlet, *J. Am. Chem. Soc.*, **98**, 2886 (1976). The α-scale of HBD increases in the order: [Solvents (1)<(2)<(3)<(4)<(5)<(5)<(6)<(7)].

5) E. M. Kosower,"Physical Organic Chemistry," John-Wiley & Sons, New York (1968), p. 303.

6) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **73**, 2700 (1951).

7) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253, 3261, 3267 (1958).

8) H. E. Haugg and A. D. Schaefer, *J. Am. Chem. Soc.*, **87**, 1587 (1965); J. F. Garst, R. A. Klein, D. Walmsley, and E. R. Zabolotny, *ibid.*, **87**, 4087 (1965); R. C. Kerber, and A. Porter, *ibid.*, **91**, 366 (1969).

9) This result is analogous to the chemical result with regard to the alkylation of phenoxides and naphthoxides [N. Kornblum, P. J. Berrigan, and J. Noble, *J. Am. Chem. Soc.*, **82**, 1257 (1960); **85**, 1141 (1963)].