Base Strength of Various Organic Oxides

C. Klofutar, F. Krašovec, and M. Kušar

Institute »Jožef Stefan«, Ljubljana, Slovenia, Yugoslavia

Received November 6, 1967

The protonation constants pK_a of various aromatic substituted organic oxides are reported. The following order of increasing basicities of the investigated organic oxides was established: sulphoxides, phosphine oxides, pyridine-N-oxides, selenoxides, arsine oxides, antimony oxides and tellurium oxides. Several effects, affecting the base strength of the investigated organic oxides, such as back donation, electronegativity of the element, its polarizability and inductive effect of the radicals bound to the element are discussed.

It was shown in a previous paper[1] that organic oxides are very effective reagents for the extraction of metal anions. Due to the fact that only protonated oxide molecules are able to extract metal anions from the aqueous phase, the extraction power strongly depends on their base strength. Hence, the basicities of organic oxides are very useful data which permit the prediction of the extraction efficiency of an individual organic oxide.

In this paper the protonation constants of various aromatic substituted organic oxides are reported. Two methods were used. The distribution method introduced by Arnett[2] is particularly suitable for the protonation constant determination of weak organic bases, which are slightly soluble in acidic aqueous solutions. With substituted pyridine-N-oxides which are relatively soluble in the mineral acid solutions the Hammett's spectrophotometric method[3] previously used by Jaffé[4] has been applied.

EXPERIMENTAL

Reagents

Commercially available triphenyl arsine oxide $(C_6H_5)_3AsO$ was dried by azeotropic distillation with benzene. After distillation the oxide was precipitated by addition of n-hexane to the remaining solution. Diphenyl selenoxide $(C_6H_5)_2SeO$, diphenylsulphoxide $(C_6H_5)_2SO$ and dibenzylsulphoxide $(C_6H_5CH_2)_2SO$ were kindly donated by Professor D. Hadži in very pure condition. Other organic oxides were also commercial products purified by distillation or recrystallisation. Triphenyl phosphineoxide $(C_6H_5)_3PO$, labelled with ^{32}P was prepared in this laboratory.[5]

The acidity function H_0 of the aqueous sulphuric acid solutions was estimated by picnometric determination of their densities at 25^0 C. From densities the real sulphuric acid concentrations in weight percent were obtained. The acidity function H_0 was then taken from the plot H_0 against weight percent of H_2SO_4 which was constructed using the data given by Paul and Long.[6]

Protonation Constants by the Distribution Method

Equal volumes of the organic and water phase were shaken in centrifuge tubes for one hour at 25^0 C. The organic phase was a solution of the investigated oxides in dichloromethane or carbon tetrachloride while the aqueous phase was a diluted

sulphuric acid solution with the known acidity function H_o. After equilibration both phases were separated by centrifugation. The concentration of the weak base in the organic phase, C_{org}, was determined spectrophotometrically or radiometrically and the one in the aqueous phase, C_{aq}, was calculated from the difference $C_{aq} = C_{tot} - C_{org}$. Knowing the values of the distribution coefficients $D = C_{org}/C_{aq}$ and the acidity functions of the corresponding aqueous sulphuric acid solutions the protonation constants of the organic oxides were calculated following to Arnett[2] by means of the equation:

$$pK_a = H_o - \log D/(K'_D - D)$$

where K'_D is the distribution constant of the organic oxide if the protonation in the water phase can be neglected.

All spectrophotometric measurements were made at 25^0 C with a spectro-photometer CF-4 (Optica, Milano) and the radiometric ones in the 10 ml. liquid counter tube, type M2H, 20th Century Electronics.

Protonation Constants by Spectrophotometric Method

The equilibrium between the protonated BH^+ and the unprotonated form B of the pyridine-N-oxides was determined spectrophotometrically after equilibrating of the water solutions containing a known and constant concentration of the oxides with the diluted sulphuric acid solutions having a known acidity function. In some cases, such as 2,5-dibromopyridine-N-oxide, the absorptivity of the unprotonated form B in comparison with the protonated form BH^+ at the wave lenght at which the protonated form exhibits maximal absorption, was very low and can be neglected. In other cases such as 2,6-dimethyl pyridine-N-oxide a correction for the absorptivity of the unprotonated form has to be taken into account. According to Hammett's calculations[3], the protonation constant can be calculated from the equation:

$$H_o = pK_a + \log [BH^+] / [B].$$

RESULTS

The experimental results are given in Fig. 1 where $\log D/(K_D' - D)$ (or $\log [B]/[BH^+]$ in the case of the pyridine-N-oxides) are plotted against the
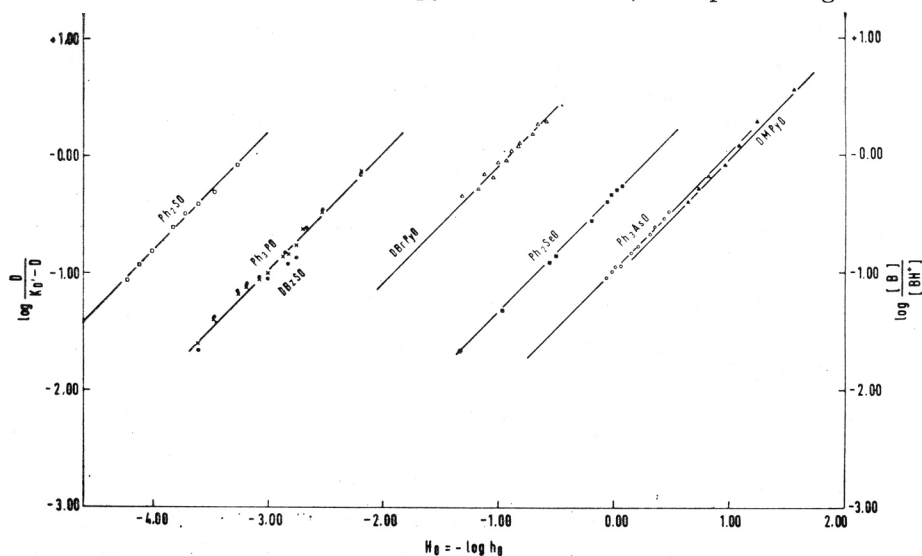

Fig. 1. Variation of the ratio between unprotonated and protonated form of the organic oxides as a function of the acidity function H_o. Symbols: Ph = phenyl, DBz = dibenzyl, DBr = dibromo, DM = dimethyl, PyO = pyridine-N-oxide.

acidity function $H_0 \cdot K_D'$ *i. e.* the distribution constant of the oxides, when the protonation in the water phase can be neglected, was calculated by the least square method from the experimentally obtained values D and $D \cdot h_0$. The points in Fig. 1 fit fairly well the straight lines with slope equal to 1 indicating the absence of the Hammett-Chapman effect[7]. The distribution coefficients were determined spectrophotometrically except in the case of triphenyl phosphineoxide when spectrophotometric as well as radiometric measurements were performed. The agreement between both determinations was quite good. However, we consider the D values obtained with radioactive Ph_3PO to be more reliable and consequently the radiometrically determined log $D/(K_D' - D)$ values are plotted in Fig. 1.

Our pK_a values are summarized together with the pK_a values of some other oxides taken from the literature in Table I. $K_i^{BH^+X^-}$ values determined previously[8] are also included in Table I.

TABLE I

Protonation Constants, pK_a, and Ionization Constants,
K_i^{BHX} *of Various Organic Oxides*

Base	$pK_{a\,(H_2O)}$	$K_i^{BH^+X^-}$
$(C_6H_5)_2SO$	— 3.19[a]	9.34
$(C_6H_5CH_2)_2SO$	— 2.03[a]	2.10×10^2
$(CH_3)_2SO$	—	3.50×10^2
$(C_2H_5)_2SO$	—	6.22×10^2
$(i\text{-}C_3H_7)_2SO$	—	6.48×10^2
$(CH_2)_5SO$	—	8.92×10^2
$(C_6H_5)_3PO$	— 2.10[a]	2.72×10^2
$(CH_3)_3PO$	0[b]	3.44×10^3
$(C_8H_{17})_3PO$	—	6.54×10^3
$C_5H_3Br_2NO$	— 0.90[a]	3.34×10^2
C_5H_5NO	0.79[c]	2.82×10^5
$C_5H_3(CH_3)_2NO$	1.02[a]	2.73×10^6
$(CH_3)_3NO$	4.65[b]	—
$(C_6H_5CH_2)_3NO$	4.70[c]	—
$(C_2H_5)_3NO$	5.13[b]	—
$(C_6H_5)_3AsO$	0.99[a]	4.66×10^6
$(C_2H_5)_3AsO$	3.71[b]	—
$(CH_3)_3AsO$	3.75[b]	—
$(C_6H_5)_2SeO$	0.35[a]	4.18×10^5
$(CH_3)_2SeO$	2.55[b]	$> 10^8$
$(CH_3)_3SbO$	5.36[b]	—
$(CH_3)_2TeO$	~ 6[b]	—
Urea	0.1[d]	$1.6 \times 10^{5(f)}$

[a] this work; [b] ref. 14; [c] ref. 13; [d] ref. 9; [e] ref. 8; [f] ref. 10.

DISCUSSION

The values of the protonation constants given in the Table show the following order of increasing basicities of the organic oxides: sulphoxides, phosphine oxides, pyridine-*N*-oxides, selenoxides, arsine oxides, antimony oxides, tellurium oxides. The same order was found by Hadži *et al.*,[8] in their investigation on ionization constants K_i^{BHX} of the organic oxides in glacial

acetic acid. In Fig. 2. log K_i^{BHX} are plotted against pK_a values of the corresponding organic oxides. Fig. 2 shows that a linear relationship between both constants exists. The K_i^{BHX} and pK_a values for urea, determined by Clark and Perrin[9] and Kolthof and Bruckenstein[10] are included in Fig. 2 and this point also fits the straight line very well. A similar linear correlation between log K_i^{BHX} and pK_a values of various organic bases was observed by Hall[11] who used titration of bases in anhydrous acetic acid in order to obtain estimates of their pK_a values in water. Only the points for pyridine-N-oxide and 2,5-dibromopyridine-N-oxide deviate from this linear relationship. It seems however, that together with 2,6-dimethylpyridine-N-oxide again they fit a straight line with a different slope. Additional experiments with other pyridine-N-oxides are planned in order to test this assumption.
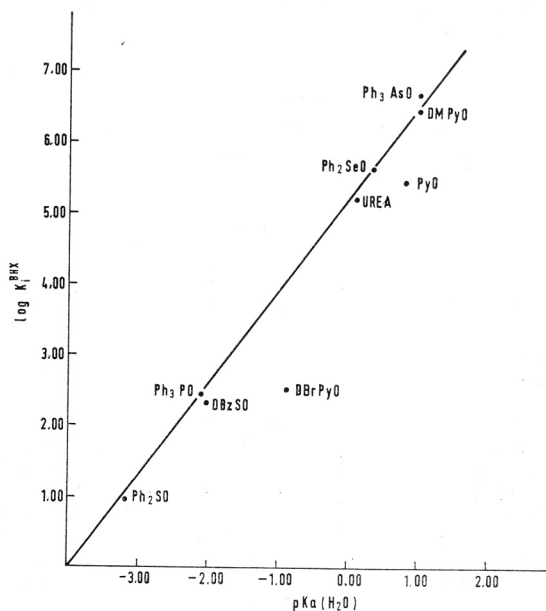

Fig. 2. Correlation between log K_i^{BHX} and pK_a of the organic oxides in question. The symbols refer to the same oxides as in Fig. 1.

The linear correlation between log K_i^{BHX} and pK_a indicates that solvatation effects do not vary widely for the bases examined and that the difference in the base strength of various organic oxides has to be attributed to the difference in electronic energy of the free molecule, R_nXO, and the protonated molecule R_nXO^+H. The principal contribution to this difference is probably due to the back donation of the oxygen p electrons to the vacant d orbitals of S, P, As, Sb, Se and Te or to the π orbitals of the pyridine ($p_\pi - d_\pi$ bonding). With aliphatic substituted N-oxides this bonding type does not exist and consequently aliphatic N-oxides are very strong bases. With increasing size and energy of d orbitals this back donation becomes less important[8]. The variation of the back donation exerts a twofold effect on the electronic energy change of the protonated and unprotonated molecule. Firstly,

with progressive decrease of the back donation the negative charge on the oxygen atom increases and secondly, the proton bound on the oxygen atom strongly inhibits the back donation. The latter is a positive energy contribution to the protonation. Consequently, the base strength of the arsine-, antimony-, selenium- and tellurium oxides is much closer to the one of the nitrogen oxides than to that of the sulphoxides and phosphine oxides where the $p_\pi - d_\pi$ bond is strongest.

Beside this back donation there are some other effects which affect the base strength of the organic oxides, such as electronegativity of the element X, its polarizability and the inductive effect of the radicals bound to the element X. Thus, for instance, the bond between arsenic or selenium and oxygen is more polar than the one between phosphorus or sulphur and oxygen. This can be due to the higher electronegativity of arsenic and selenium[12] which is affected by the transition from eight to eighteen electronic structure. All the effects mentioned above cause a higher electron density around the oxygen atom and consequently a higher donation power. On the other hand, the difference in the base strength of the sulphoxides and phosphine oxides can probably be due to the different electronegativity of sulphur and phosphorus and to the different strength of the back donation.

From the Table the inductive effect of the radicals bound to the element X can be deduced. It may be seen that aromatic organic oxides are always much weaker bases that the corresponding aliphatic compounds. Since the conjugation through sulphur and phosphorus is not probable, the reason for the different basicities of the aromatic and aliphatic oxides must be sought in the different electronegativities of sp^2 and sp^3 carbon. A negative inductive effect can be observed with 2,5-dibromopyridine-N-oxide while with 2,5-dimethylpyridine-N-oxide two methyl groups exhibit a positive inductive effect.

REFERENCES

1. F. Krašovec and C. Klofutar, *Solvent Extraction Chemistry*, North-Holland Publishing Comp., Amsterdam 1967, p. 509.
2. E. M. Arnett, C. Y. Wu, J. N. Andreson, and R. D. Bushick, *J. Am. Chem. Soc.* **84** (1962) 1674.
3. L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.* **54** (1932) 2721.
4. H. H. Jaffé and G. O. Doak, *J. Am. Chem. Soc.* **77** (1955) 4441.
5. F. Krašovec, M. Ostanek, and C. Klofutar, *Anal. Chim. Acta* **36** (1966) 431.
6. M. A. Paul and F. A. Long, *Chem. Rev.* **51** (1957) 1.
7. L. P. Hammett and P. R. Chapman, *J. Am. Chem. Soc.* **56** (1934) 1282.
8. D. Hadži, C. Klofutar, and S. Oblak, *J. Chem. Soc.* in press.
9. J. Clark and D. D. Perrin, *Quart. Rev.* **28** (1964) 295.
10. I. M. Kolthoff and S. Bruckenstein, *J. Am. Chem. Soc.* **78** (1956) 1.
11. N. E. Hall, *J. Am. Chem. Soc.* **52** (1930) 5115.
12. R. T. Sanderson, *Chemical Periodicity*, Reinhold Publishing Corporation. New York 1961, Charter VI.
13. T. Kubota, *J. Am. Chem. Soc.* **87** (1965) 458.
14. P. Nylén, *Z. Anorg. Allg. Chem.* **246** (1941) 227.

IZVLEČEK

Bazičnost organskih oksidov

C. Klofutar, F. Krašovec in M. Kušar

Določili smo protonacijske konstante pK_a različnih, aromatsko substituiranih organskih oksidov. Ugotovili smo, da bazičnost organskih oksidov narašča v naslednjem vrstnem redu: sulfoksidi, fosfinoksidi, piridin-N-oksidi, selenoksidi, arzinoksidi, antimonoksidi in teluroksidi. Tolmačili smo vpliv različnih faktorjev, ki določajo bazičnost preiskovanih organskih oksidov in sicer vpliv povratne vezi, elektronegativnosti in polarizabilnosti elementa ter induktivni vpliv substituent.

ODSEK ZA FIZIKALNO KEMIJO
NUKLEARNI INSTITUT »JOŽEF STEFAN«
LJUBLJANA