

4. R. E. Steiger, *J. Org. Chem.*, **9**, 396 (1944).
5. P. R. Levy and H. Stephen, *J. Chem. Soc.*, 985 (1956).
6. N. M. Émanuél' and D. G. Knorre, *Course in Chemical Kinetics* [in Russian], Vysshaya Shkola (1974).
7. M. I. Vinnik and N. B. Librovich, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2211 (1975).
8. N. B. Librovich, V. L. Maiorov, and V. A. Savel'ev, *Dokl. Akad. Nauk SSSR*, **225**, 1358 (1975).
9. K. Jates, I. B. Stevens, and A. K. Katritzky, *Can. J. Chem.*, **42**, 1957 (1964).
10. P. P. Nechaev, *Dissertation*, Moscow (1975).
11. A. Albert and E. Sargent, *Ionization Constants for Acids and Bases* [Russian translation], Khimiya (1964), p. 139.
12. *Chemists' Handbook* [in Russian], Vol. 3, Khimiya (1964), p. 961.
13. K. J. Morgan and A. M. Turnes, *Tetrahedron*, **25**, 915 (1969).
14. S. Hoshino, H. Hosoya, and S. Nagakura, *Can. J. Chem.*, **44**, 1961 (1966).
15. Yu. R. Siigur and Yu. L. Khaldna, *Reakts. Sposobn. Org. Soedin.*, **7**, 197 (1970).
16. N. C. Deno, C. U. Pittman, and M. I. Wisotsky, *J. Am. Chem. Soc.*, **86**, 4370 (1964).
17. W. S. Schubert, J. Donohue, and J. D. Gardnes, *J. Am. Chem. Soc.*, **76**, 9 (1954).
18. L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **55**, 1900 (1933).
19. H. Zimmerman and H. Grisenfeldes, *Z. Electrochem.*, **65**, 368 (1961).
20. R. V. Rabiger and M. M. Joullic, *J. Org. Chem.*, **29**, 476 (1964).
21. N. B. Librovich and M. I. Vinnik, *Zh. Fiz. Khim.*, **50**, 150 (1976).

## AMIDE IONIZATION AND THE $H_A$ ACIDITY FUNCTION

N. G. Zarakhani, P. P. Nechaev,  
and G. E. Zaikov

UDC 541.124.7:547.582.4:543.241.5

The thermodynamic properties of the medium and the equilibrium state of the system are not generally taken into account in spectrophotometric determinations of basicity constants of weak organic bases in aqueous solutions of strong acids. In fact, weak-base ionization is essentially considered as an instance of proton addition



It has, however, been shown both spectrophotometrically [1-6] and kinetically [1] that the protonated form of the weak base is in equilibrium with ion pairs, complexes, and other particle types as well.

It has been suggested [7, 8] that hydrated proton complexes form during the ionization of certain carbonyl compounds, in particular carboxylic acid anilides, in strong acid solutions.

There is convincing evidence that protons in aqueous solutions of strong acids firmly solvate with two water molecules each, to form  $H_5O_2^+$  ions with characteristic IR spectrum [9]. Practically all of the protons are in this form in concentrated acid systems with excess water,  $H_3O^+$  ions being the rarity, earlier beliefs to the contrary.

The  $H_A$  acidity function has been used with amide indicators [10, 11] to show the inapplicability of the  $H_0$  function for quantitatively describing the mechanism of amide ionization through the equilibrium of (1).

Since the spectrophotometric method does not generally lead to a direct determination of the concentration of the ionized weak-base form, and requires a mass balance equation in order to set up a particle balance, the concentration of the ionized form of the weak base is generally determined as the difference between the analytic concentration ( $C_0$ ) and the concentration of the un-ionized form at equilibrium ( $C_B$ ), the latter determined experimentally. To us this seems to be a purely formal approach to the problem, the fact that the mechanism of weak-base ionization has already been predetermined as proton addition with  $BH^+$  formation excluding all other possibilities from consideration. It might, however, be supposed that amide ionization in strong acids,  $H_2SO_4$ , in particular, proceeds through the following reversible scheme:

---

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 3, pp. 568-571, March, 1978. Original article submitted November 4, 1976.

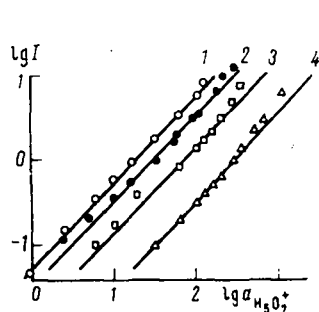


Fig. 1

Fig. 1. Variation of log I with log  $a_{H_5O_2^+}$ : 1) amide of 2-pyrrolecarboxylic acid; 2) 4-methoxybenzamide; 3) 3,4,5-trimethoxybenzamide; 4) 3-nitrobenzamide.

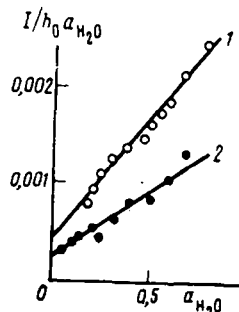


Fig. 2

Fig. 2. Variation of  $I/h_0 a_{H_2O}$  with  $a_{H_2O}$ : 1) 3-nitrobenzamide; 2) 3,5-dinitro-4-methylbenzamide.



It has been shown in [12, 13] that  $h_0$ , the Hammett acidity, or more exactly, the proton activity equal to the Hammett acidity ( $a_{H^+} = h_0$ ) can serve as a thermodynamic measure of solution acidity. Thus, the thermodynamic activities of  $H_5O_2^+$  and  $H_3O^+$  can be represented by

$$a_{H_5O_2^+} = h_0 a_{H_2O}^2 \text{ and } a_{H_3O^+} = h_0 a_{H_2O}$$

If the molar absorption coefficients of the ionized forms  $B \cdot H^+ \cdot 2H_2O$ ,  $B \cdot H^+ \cdot H_2O$ , and  $B \cdot H^+$  are identical or close in value, which seems likely, it would be reasonable to assume that the ionization ratio could be represented by an equation of the form

$$I = \frac{[C_{B \cdot H^+ \cdot 2H_2O} + C_{B \cdot H^+ \cdot H_2O} + C_{B \cdot H^+}]}{C_B} = \frac{h_0 a_{H_2O}^2 f_B}{K_1 \cdot f_{B \cdot H^+ \cdot 2H_2O}} + \frac{h_0 a_{H_2O} f_B}{K_2 \cdot f_{B \cdot H^+ \cdot H_2O}} + \frac{h_0 f_B}{K_3 f_{B \cdot H^+}} \quad (5)$$

We have, therefore, accepted the validity of the Hammett hypothesis here, considering the ratio of the activities of the ionized and un-ionized forms to be the same for each of the various weak-base species

$$\frac{f_{B \cdot H^+ \cdot 2H_2O}}{f_B} = \frac{f_{C \cdot H^+ \cdot 2H_2O}}{f_C} = \frac{f_{D \cdot H^+ \cdot 2H_2O}}{f_D} = \dots$$

$$\frac{f_{B \cdot H^+ \cdot H_2O}}{f_B} = \frac{f_{C \cdot H^+ \cdot H_2O}}{f_C} = \frac{f_{D \cdot H^+ \cdot H_2O}}{f_D} = \dots$$

We have, in turn, used these relations to analyze the  $H_A$  acidity function for benzamide derivatives reported in [10, 11].

It can be seen from Fig. 1 that the plot of the log I vs log  $a_{H_5O_2^+}$  had a slope of one. The indication here is that the ionization of the amides in question was essentially a matter of  $H_5O_2^+$  ion addition. Processes (3) and (4) were therefore neglected here. An exception was made in the case of 3-nitrobenzamide, for which Eq. (5) took the form

$$\frac{I}{h_0 a_{H_2O}} = \frac{a_{H_2O}}{K_1} + \frac{1}{K_2}$$

the ionization process being described by Eqs. (2) and (3). It can be seen from Fig. 2 that similar processes were involved in the ionization of 3,5-dinitro-4-methylbenzamide.

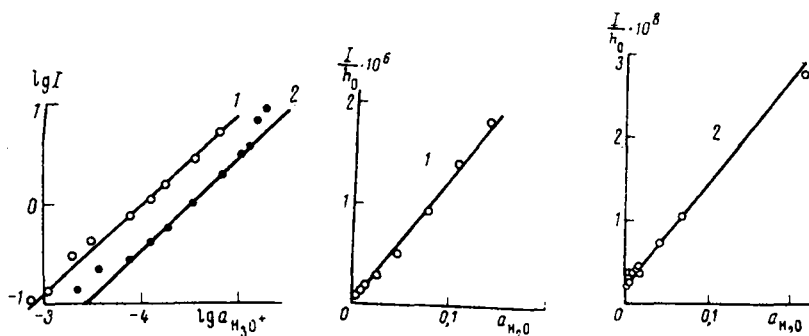


Fig. 3

Fig. 4

Fig. 3. Variation of  $\log I$  with  $\log a_{H_3O^+}$ : 1) 2,3,6-trichlorobenzamide; 2) 2,4-dichloro-3,5-dinitrobenzamide.

Fig. 4. Variation of  $I/h_0$  with  $a_{H_2O}$ : 1) 2,4,6-trinitrobenzamide; 2) phenazine 5,10-dioxide.

TABLE 1. Equilibrium Constants for Reactions (2), (3), and (4)

Amide	$pK_1$	$pK_2$	$pK_3$
Amide of 2-pyrrolecarboxylic acid	-1,24	—	—
4-Methoxybenzamide	-1,45	—	—
3,4,5-Trimethoxybenzamide	-1,81	—	—
3-Nitrobenzamide	-2,42 *	—	—
	-2,60	-3,36	—
5,3-Dinitro-4-methylbenzamide	-2,89	-3,57	—
2,3,6-Trichlorobenzamide	—	-3,97	—
2,4-Dichloro-3,5-dinitrobenzamide	—	-4,44	—
2,4,6-Trinitrobenzamide	—	-4,93	-7,52
Phenazine 5,10-dioxide	—	-6,90	-8,70

\* Obtained from Fig. 1.

The ionization of 2,3,6-trichlorobenzamide and 2,4-dichloro-3,5-dinitrobenzamide was largely a matter of addition of the  $H_3O^+$  hydronium ion (Fig. 3). Here the slope of the  $\log I$  vs  $\log a_{H_3O^+}$  plot was again close to one.

The ionization of 2,4,6-trinitrobenzamide and phenazine 5,10-dioxide was a matter of the addition of a proton and a hydronium  $H_3O^+$  ion, a process described by Eq. (5) in reduced form

$$\frac{I}{h_0} = \frac{a_{H_2O}}{K_2} + \frac{1}{K_3}$$

Here the equilibrium of (2) had essentially no effect on the ionization process. Figure 4 shows  $I/h_0$  vs  $a_{H_2O}$  plots for these two amides. The fact that each of these plots was linear opens the possibility of determining the ionization constants graphically.

The mechanism proposed here gives a quantitative description of amide ionization which can be used as a basis for developing the  $H_A$  acidity function. The data of Table 1 show that the effects from reversible dehydration of the ionized form, with the attendant sharp reduction in the thermodynamic activity of water, were felt more and more strongly as the amide basicity diminished.

It is our opinion that Eq. (5) gives a general description of amide ionization. Amide protonation can result from addition of  $H_5O_2^+$ ,  $H_3O^+$ , and  $H^+$  ions, depending on the acid-to-water ratio in the system. It is clear that steric hindrances reduce the possibility of  $H_5O_2^+$  ionization of N-substituted amides and anilides of various structures.

## CONCLUSIONS

A description of the ionization of benzamide derivatives, applicable over a wide range of parameter values and acid concentrations, can be set up in terms of the Hammett acidity function and the thermodynamic activity of water.

## LITERATURE CITED

1. M. I. Vinnik, N. G. Zarakhani, I. M. Medvedskaya, and N. M. Chirkov, Dokl. Akad. Nauk SSSR, 126, 1300 (1959); M. I. Vinnik and N. G. Zarakhani, Zh. Fiz. Khim., 34, 2671 (1960); 38, 907 (1964); Dokl. Akad. Nauk SSSR, 152, 1147 (1963); N. G. Zarakhani, V. V. Budylna, and M. I. Vinnik, Zh. Fiz. Khim., 39, 1561, 1863 (1965); N. G. Zarakhani and M. I. Vinnik, Zh. Fiz. Khim., 40, 333 (1966); M. I. Vinnik and N. G. Zarakhani, Usp. Khim., 36, 167 (1967).
2. N. B. Librovich, N. G. Zarakhani, and M. I. Vinnik, Zh. Fiz. Khim., 44, 395 (1972).
3. Yu. K. Karasevich, N. B. Librovich, and M. I. Vinnik, Zh. Fiz. Khim., 47, 2017 (1973).
4. N. B. Librovich, Yu. K. Karasevich, and M. I. Vinnik, Zh. Fiz. Khim., 47, 2294 (1973).
5. M. I. Vinnik, L. D. Abramovich, L. G. Yudin, and V. A. Budylin, Zh. Fiz. Khim., 44, 2845 (1970).
6. A. G. Zhigulin, N. B. Librovich, L. G. Yudin, A. N. Kost, and M. I. Vinnik, Zh. Obshch. Khim., 12, 606, 875 (1976).
7. M. É.-É. Tamme, Yu. L. Khaldna, and Kh. I. Kuura, Reakts. Sposobn. Org. Soedin., 8, 1131 (1971); Kh. I. Kuura, M. É.-É. Tamme, and Yu. L. Khaldna, Reakts. Sposobn. Org. Soedin., 8, 1201 (1971).
8. M. É.-É. Tamme, Yu. L. Khaldna, and Kh. I. Kuura, Reakts. Sposobn. Org. Soedin., 9, 617, 637 (1972).
9. N. B. Librovich, V. D. Maiorov, and V. A. Saevl'ev, Dokl. Akad. Nauk SSSR, 225, 1358 (1975).
10. K. Yates, J. B. Stevens, and A. R. Katritzky, Can. J. Chem., 42, 1957 (1964).
11. C. D. Johnson and A. R. Katritzky, J. Chem. Soc. B, 1235 (1967).
12. Yu. F. Rybkin and N. F. Shevchenko, Élektrokhimiya, 1, 46 (1965).
13. M. J. Vinnik and N. B. Librovich, Tetrahedron, 22, 2945 (1966).

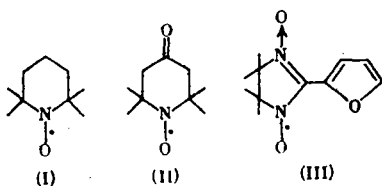
## OXIDATION OF NITROXYL RADICALS BY XENON DIFLUORIDE

V. A. Golubev, V. V. Solodova,  
N. N. Aleinikov, B. L. Korsunskii,  
É. G. Rozantsev, and F. I. Dubovitskii

UDC 542.943:541.515:546.295'161

Nitroxyl radicals can be converted into the analogous oxoammonium salts through one-electron loss [1-5]. Xenon difluoride shows clearly expressed oxidizing properties [6, 7]. Study of the interaction of nitroxyl radicals with  $\text{XeF}_2$  should furnish information concerning the action of the latter as a one-electron oxidizing agent, possibly giving rise, at the same time, to the synthesis of oxoammonium fluorides which have not yet been described.

Experiments showed that  $\text{XeF}_2$  would readily interact with the nitroxyl radicals (I)-(III) under ordinary conditions, Xe being quantitatively liberated in the course of the reaction



Branch of the Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 572-576, March, 1978. Original article submitted December 6, 1976.