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EQUILIBRIUM CH ACIDITY OF ARYLACETYLENES IN DIMETHYL SULFOXIDE

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Quantitative data on the equilibrium CH acidity of terminal acetylenes are scanty. The pK of a number of heteroatomic acetylenes were determined in DMSO and 1,2-dimethoxyethane [1, 2], and of the methoxy-, dimethylamino-, and individual alkylacetylenes [3], and of ethynyl-substituted nitrogen heterocycles [4] were determined in DMSO. Of the aryl derivatives only phenylacetylene was studied in this respect, whose pK was determined in DMSO (22.6 [3], 28.8 [5]), 1,2-dimethoxyethane (23.7 [1]), cyclohexylamine (23.2 [6]), diethyl ether (21 [7], 17.2 [8]), and diglyme (25.1 [8]).

We studied the equilibrium CH acidity of a series of para-substituted phenylacetylenes and some ethynyl derivatives of naphthalene, pyridine, and pyrimidine in DMSO. The pK were measured by the usual transmetallation method [9, 10]. The use of the highly polar DMSO as the solvent permits avoiding a superimposition of the effects of ionic association on the protolytic equilibrium whose effects are responsible for the divergences in estimating the pK of phenylacetylene in different solvents [8] (see [5] for the possible reasons for the differences in the pK in DMSO). The obtained results are given in Table 1.

The acidity of the studied compounds increases with increase in the electron-acceptor capacity of the aryl group in the order: phenyl < naphthyl < pyridyl < pyrimidyl. Here the pK value found by us for phenylacetylene (IV) (29.1) coincides with the pK value obtained in [5] (taking into account the difference between the acidity scales employed in [5, 10], which in the range pK >20 is 0.3 pK units [8]), which confirms the error of estimating the acidity of (IV) in [3]. An excellent linear relationship between the pK and the Hammett σ constants of the para substituents is fulfilled for the series of substituted phenylacetylenes (I)-(VII). For the NMe_2 group we adopted the Jaffe [11] value of $\sigma = -0.60$ as best satisfying the Hammett equation for a number of the reaction series and leveling to a certain degree the difference in the disturbing effect of the direct conjugation of this substituent and the unsaturated groups, containing the reaction center.

$$pK = (28.96 \pm 0.03) - (3.04 \pm 0.12)\,\sigma \quad s = 0.09;\ r = 0.996;\ n = 7$$

We were unable to measure the acidity of 4-nitrophenylacetylene and thus include in the correlation a compound with a strong acceptor substituent due to side processes, which complicate the transmetallation reaction in this case (an attempt to determine the pK of 1-ethynylanthracene proved unsuccessful for the same reason). The chemistry of these side reactions, which lead to the formation of colored products, was not studied. The rate with which the

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TABLE 1. Equilibrium CH Acidity (pK) of Substituted Acetylenes (RC≡CH) and Equilibrium Constants (K_p) of Reaction of RC≡CH with Potassium Salts of Indicator CH Acids in DMSO.

Compound	R	pK	Indicator (pK) [10]	K_p^*
(I)	$4\text{-}Me_2NC_6H_4$	30,8	Triphenylmethane (31.1)	1,9±0,1
(II)	$4\text{-}MeOC_6H_4$	29,7	p-Biphenylyldiphenylmethane (29.7)	1,0±0,1
(III)	$4\text{-}MeC_6H_4$	29,5	9-Phenylxanthene (28.3)	0,065±0,007
(IV)	Ph	29,1	p-Biphenylyldiphenylmethane	0,16±0,02
(V)	$4\text{-}FC_6H_4$	28,7	9-Phenylxanthene	0,37±0,03
(VI)	$4\text{-}BrC_6H_4$	28,3	»	1,0±0,1
(VII)	$4\text{-}ClC_6H_4$	28,2	»	1,3±0,1
(VIII)	$2\text{-}C_{10}H_7$	28,8	»	0,31±0,02
(IX)	$1\text{-}C_{10}H_7$	28,4	»	0,77±0,05
(X)	$3\text{-}C_5H_4N$	28,0	»	1,9±0,4
(XI)	$4\text{-}C_5H_4N$	26,9	1,1,3,3-Tetraphenylpropene (26.2)	0,22±0,06
(XII)	$2\text{-}C_4H_3N_2$	25,8	1,1,3,3-Tetraphenylpropene	2,3±0,2

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*Average of ~5-6 measurements.

acetylene and indicator (or only the indicator) were consumed in them is quite great, and determination with an acceptable accuracy of the equilibrium concentrations of the reactants during transmetallation becomes impossible. Nevertheless, the studied reaction series was expanded via the ethylnylazines (X)-(XII), the N atoms in which can be regarded as being equivalents of the acceptor groups in the phenyl ring with σ values of 0.55, 0.44, and 0.78, which were determined in DMSO respectively for the 2-, 3-, and 4-aza groups [12]. In essence, the acidity of (X)-(XII) satisfies the established linear function pK vs. σ, which, taking into account the data for the combination of substituted phenylacetylenes and ethynylazines, is described by the equation

$$pK = (29{,}0 \pm 0{,}05) - (2{,}84 \pm 0{,}09)\,\sigma' \quad s = 0{,}14;\ r = 0{,}0996;\ n = 10$$

A fast shift of the equilibrium position of the transmetallation due to the effect of the side processes does not permit regarding the pK value, obtained in our experiments for 2-ethynylpyridine (~28), as being reliable, and it was not used in the calculations.

The existence of a linear pK vs. σ relationships, which is also valid for such substituents as NMe_2 and OMe, can apparently testify to the effect of the conjugation of the aryl group with the triple bond on the acidity of arylacetylenes, i.e., to the difference of this conjugation in the acetylide anion and the undissociated acetylene. It is not excluded that this is also indicated by an increase in the CH acidity when going from phenyl- (IV) to naphthylacetylenes (VIII) and (IX). A stabilization of carbanions via p_π–d_π conjugation was also previously postulated for heteroatomic acetylenes [1].

At the same time, as follows from the correlation equation, the acid-base equilibrium of arylacetylenes, in which the acetylide anion takes part, which has an unshared pair of electrons on the sp orbital, is fairly insensitive to the character of the substituents in the aromatic ring: The value of the reaction constant for it is ~4 times smaller than for the analogous equilibrium of forming resonance-stabilized carbanions of the benzyl type from substituted toluenes (ρ ~ 12) [13].

A confirmation of the validity of the conclusion on the contribution made by the direct conjugation of the acetylene group with the substituent in the ring to the acidity of acetylenes would be the absence of a correlation of the pK values with the σ^0 constants of the substituents. However, it proved that within the limits of the studied series of phenylacetylenes (I)-(VII) the function pK vs. σ^0 is linear and is an excellent correlation, whose coefficient is only slightly smaller than for the function pK vs. σ.

$$pK = (29{,}17 \pm 0{,}05) - (3{,}50 \pm 0{,}20)\,\sigma^0 \quad s = 0{,}13;\ r = 0{,}992;\ n = 7$$

The low sensitivity of the correlation parameters (r, s) to the choice of the scale for the constant of the substituents is probably explained by the limited set of studied phenylacetylenes and the relatively low value of the reaction constant ρ when the total contribution made by the direct conjugation effect to the CH acidity of arylacetylene compounds is small.

EXPERIMENTAL

Ethynyl compounds (II) [14], (III) [15], and (V)-(VII) [14], and 1-ethynylanthracene [16] were synthesized by the reaction of methyl aryl ketones with PCl_5 and dehydrochlorination of the formed chloro derivatives with either $NaNH_2$ in NH_3 or KOH in EtOH, while acetylenes (I) [17], (VIII), (IX) [18], (X), (XI) [19], (XII) [20], 4-nitrophenylacetylene [14], and 2-ethynylpyridine [21] were synthesized by the condensation of aryl halides with 2-methyl-3-butyn-2-ol and subsequent alkaline cleavage of the tertiary arylacetylenic alcohols [22]. The constants of compounds (I)-(XII) coincided with the literature data. To measure the pK the compounds were purified by chromatography, recrystallization, and either sublimation or fractional distillation in vacuo.

The equilibrium constants of the transmetallation reactions were determined spectrophotometrically on an SF-4A instrument using a one-piece vacuum apparatus and carefully dried DMSO. The previously described method [10] for measuring the pK was used.

CONCLUSIONS

1. We measured the equilibrium CH acidity in DMSO of a series of para-substituted phenylacetylenes, 1- and 2-ethynylnaphthalene, 3- and 4-ethynylpyridines, and 2-ethynylpyrimidine.

2. A linear correlation between the pK and the Hammett σ constants of the substituents is fulfilled in the series of para-substituted phenylacetylenes and ethynylazines.

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