A CONTRIBUTION TO GAS PHASE IONIZATION OF *para*-
-HYDROXYBENZOIC ACID: AN LCAO-MO-SCF TREATMENT
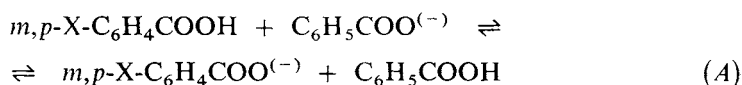
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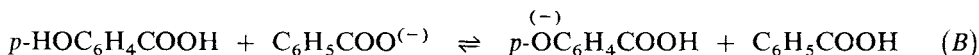*Prague Institute of Chemical Technology, 166 28 Prague 6*

By means of the ab initio MO calculations using the STO-3G basis set augmented with diffuse p functions accompanied by semi-empirical MNDO calculations, it is demonstrated that the carboxylic group ionization in the isodesmy (A), X = p-OH, is energetically preferred to the phenolic group ionization in the process (B). The reasons of the earlier incorrect interpretations regarding the gas phase acidity of p-hydroxybenzoic acid $(a,s-II)$ are discussed.

The study of Gibbs' energy changes accompanying the isodesmic gas phase equilibria

$$m,p\text{-X-C}_6\text{H}_4\text{COOH} + \text{C}_6\text{H}_5\text{COO}^{(-)} \rightleftharpoons$$
$$\rightleftharpoons m,p\text{-X-C}_6\text{H}_4\text{COO}^{(-)} + \text{C}_6\text{H}_5\text{COOH} \qquad (A)$$

has led to the conclusion[1] that the data for X = p-OH were considerably deviated from the regression line in the correlation of the Gibbs energies with the Hammett σ_X parameters. An analogous deviation was observed[2] in the correlation of the theoretical substituent effect calculated by an ab initio MO method using the STO-3G (x) basis set augmented with diffuse p functions on the O centres in COOH and $\text{COO}^{(-)}$ groups. These findings led to the assumption[1,2] that the preferred dissociation

$$p\text{-HOC}_6\text{H}_4\text{COOH} + \text{C}_6\text{H}_5\text{COO}^{(-)} \rightleftharpoons p\text{-}\overset{(-)}{\text{O}}\text{C}_6\text{H}_4\text{COOH} + \text{C}_6\text{H}_5\text{COOH} \qquad (B)$$

took place instead of the equilibrium (A) for X = p-OH.

The aim of this paper was to reinvestigate, within the framework of the STO-3G basis, to what extent the theoretical conclusion[2] is influenced by the AO basis set contraction, since a direct experimental evidence in support of the equilibrium (B) can hardly be provided by means of available techniques.

CALCULATIONS

All the non-empirical calculations were carried out using a modified version of the Gaussian 76 program[3]. The CNDO/2 models optimized with respect to all degrees of freedom[4] were

used as the starting molecular geometries. Three series of calculations were applied and mutually confronted, namely those involving (i) the simple STO-3G basis set, (ii) the STO-3G (α_1) basis set augmented with the identical diffuse $2p$ functions having the coefficient $\alpha_1 = 0.134$ at all the O centres, (iii) the STO-3G ($\alpha_1\alpha_2$) basis set augmented with different $2p$ functions having the same α_1 coefficient at the O centres in carboxylic COOH or $COO^{(-)}$ groups and the value $\alpha_2 = 0.144$ at the O centres in phenolic OH and $O^{(-)}$ groups. The values of the α_1 and α_2 coefficients were optimized by means of the SCF models of acetate ion $CH_3COO^{(-)}$ and methoxide ion $CH_3O^{(-)}$, respectively, so as to obtain the lowest energies for both the particles. The semi-empirical MNDO calculations were performed using the standard program[5] with the same molecular geometries as in the non-empirical treatments.

RESULTS AND DISCUSSION

The energy change accompanying the reaction (A) can be considered to be the theoretical substituent effect[6] of the X group; in our case ($X = p$-OH) it is given by the expression

$$\delta \, \Delta E_{p\text{-OH}} = \Delta E_{p\text{-OH}} - \Delta E_{H} , \tag{1}$$

where ΔE_{p-OH} and ΔE_H denote the differences between the calculated energies of the ionized and free forms of p-hydroxybenzoic acid ($IV, a, s\text{-}II$) and benzoic acid (III, I), respectively.
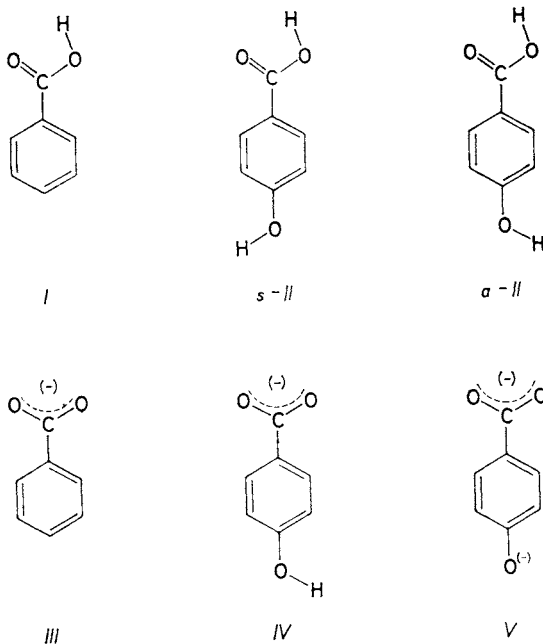
If, in the calculation, the energy of the ionized form *IV* is replaced by that of the alternative ion *V*, then the $\delta \Delta E_{p\text{-OH}}$ value corresponds to the alternative ionization (*B*). Both theoretical energy characteristics can then be compared with the experiment by means of the MIMAT theorem defined by Eq. (2) for the case of *meta* and *para* substituted benzoic acids[2]:

$$\delta \Delta E_{p\text{-OH}} = 0.842(\Delta G_{p\text{-OH}} - \Delta G_H) + 2.35, \tag{2}$$

where the ΔG_{p-OH} and ΔG_H values are the Gibbs energies determined[1] for the gas phase ionizations of acids *I* and *II*, respectively, at 600 K. With regard to the high degree of desmicity[7] of both the equilibrium processes (*A*) and (*B*) we can assume a negligible effect of correlation energy. Hence we have restricted our calculations of energy characteristics to the SCF level only (see the E_{SCF} energy in Table I). Within the non-empirical treatment we have investigated the effect of the STO-3G basis set augmentation in the order STO-3G → STO-3G(α) → STO-3G(α_1) → → STO-3G($\alpha_1\alpha_2$). In addition, the corresponding MNDO calculation has been carried out for comparison. The calculated data are given in Table II.

As expected, from Table I it follows that the STO-3G energy of negatively charged particles *III* to *V* is underestimated more distinctly (1 050 to 1 313 kJ mol^{-1}) than the energy of the non-charged acids *I* and *II* (525 to 790 kJ mol^{-1}) as compared with the respective STO-3G(α_1) values. The transition to the STO-3G($\alpha_1\alpha_2$) basis set causes smaller energy effects (c. 2.6 kJ mol^{-1}), comparable for the charged and non-charged particles *II*, *IV*, and *V*. This finding can easily be interpreted: the extension of the diffuse functions to all the atomic centres possessing lone electron pairs (O centres) is more important than the individual differences between the optimized values of the coefficients α_1 and α_2. As far as the conformational equilibrium *s-II* ⇌ ⇌ *a-II* is concerned, the decrease of the energy difference between both conformers from 2.6 kJ mol^{-1} to 0.26 kJ mol^{-1} is caused by the introduction of the diffuse functions, and the optimization of α_1 and α_2 values does not change the mutual energy preferences of both the rotational isomers.

The introduction of the experimental $\Delta G_{p\text{-OH}}$ and ΔG_H data[1] into Eq. (2) gives the energy difference $\delta \Delta E_{p\text{-OH}} \doteq 13.6$ kJ mol^{-1}. The comparison of analogous theoretical energies for the processes (*A*) and (*B*) in Table II shows that they converge to the above-mentioned $\delta \Delta E_{p\text{-OH}}$ value only in the first case (*A*). Although the energy change calculated for the process (*A*) with application of the simple STO-3G basis set still seems to be qualitatively incorrect, introduction of the diffuse functions α_1 or α_1 and α_2 leads to the correct exoergic change. The use of the double optimization of the α_1 and α_2 coefficients shifts the theoretical energies by about 2.4 kJ mol^{-1} nearer to the experimental value $\delta \Delta G = -17$ kJ mol^{-1}. From the nature of the ab initio MO method it follows that any further AO basis set extension would undoubtedly cause further decrease of the $\delta \Delta E_{p\text{-OH}}$ energies calculated for equili-

brium (A) and they approach to the "experimental" value of $-17\ \mathrm{kJ\ mol^{-1}}$. Contrary to this tendency, the $\delta\ \Delta E_{p\text{-OH}}$ energies calculated for the process (B) tend to increase as far as the endoergic region, and their comparison with the above-mentioned experimental energy, therefore, loses any physical meaning. Therefore, the results of our calculations given in Table II can be considered as a conclusive argument in favor of the real existence of the gas phase ionization (A) under the conditions used[1]. The alternative ionization (B) can then be admitted as an only minor competitive process which does not substantially influence the reaction energetics.

TABLE I

The calculated total $-E_{\mathrm{SCF}}$ energies of the species studied. All the data are in dimensionless units E_{tot}/h $(h = 2\ 625 \cdot 5\ \mathrm{kJ\ mol^{-1}})$

Method	Species					
	I	*s-II*	*a-II*	*III*	*IV*	*V*
MNDO[a]	1 623·63318	1 946·02086	1 946·01135	1 610·10427	1 932·42293	1 933·23848
STO-3G	412·966199	486·807500	486·806651	412·215395	486·053020	486·087979
STO-3G (α)[b]	413·20436	487·04786	487·04734	412·62405	486·46530	—
STO-3G (α_1)	413·204362	487·146220	487·146338	412·624050	486·571023	486·558296
STO-3G $(\alpha_1\alpha_2)$	—	487·147660	487·147540	—	486·572223	486·558645

[a] For semi-empirical data $h = 96\cdot4867\ \mathrm{kJ\ mol^{-1}}$; [b] the diffuse functions for —COOH and —COO$^{(-)}$ groups only, taken from ref.[2].

TABLE II

The calculated $\delta\ \Delta E$ energies for isodesmic equilibria (A) and (B). All the data in $\mathrm{kJ\ mol^{-1}}$

Method	$(A)^c$	$(A)^b$	$(B)^a$	$(B)^b$
MNDO	$+6\cdot7$	$+5\cdot7$	$-72\cdot0$	$-73\cdot0$
STO-3G	$+9\cdot7^c$	$+7\cdot4$	$-82\cdot1$	$-84\cdot4$
STO-3G (α_1)	$-13\cdot4^d$	$-13\cdot1$	$+18\cdot5$	$+20\cdot3$
STO-3G $(\alpha_1\alpha_2)$	$-14\cdot3$	$-14\cdot6$	$+21\cdot4$	$+21\cdot0$
Experiment		$-13\cdot6^e$		

[a] For *syn*-conformers *s-II*; [b] for *anti*-conformers *a-II*; [c] the value of $+3\cdot14\ \mathrm{kJ\ mol^{-1}}$ is reported in ref.[9]; [d] the value of $+5\cdot90\ \mathrm{kJ\ mol^{-1}}$ was calculated[2] with application of diffuse functions for O-centres of carboxylic group only; [e] calculated from experimental $\delta\ \Delta G$ energies according to the MIMAT theorem[2].

Moreover, from the data of Table II it follows that the theoretical level of predictions based on the (relatively) most sophisticated semi-empirical MNDO method appears to be only slightly appropriate, as compared with the unsatisfactory non-empirical STO-3G treatment. Consequently, the MNDO method can hardly be used for correct quantitative considerations of energetics of chemical transformations of (A) or (B) types.

The reason for the different signs of the $\delta \Delta E_{p\text{-OH}}$ values obtained from STO-3G and STO-3G$(\alpha_1\alpha_2)$ calculations becomes evident when the changes of individual terms in Eq. (1) are evaluated.

The introduction of the diffused functions into the dioxygen groups —COOH and —COO$^{(-)}$ exhibits a more distinct effect on the E_{SCF} energy decrease than in the case of the monooxygen groups —OH and —O$^{(-)}$. Consequently, the ΔE_H energy decrease is 446·1 kJ mol^{-1}, whereas the $\Delta E_{p\text{-OH}}$ energy decreases by as much as about 470 kJ mol^{-1}, and the resulting $\delta \Delta E_{p\text{-OH}}$ values necessarily become more negative. The decrease of the $\delta \Delta E_{p\text{-OH}}$ term during the ionization of the phenolic hydroxylic group in the process (B) is then considerably lower (about 340 kJ mol^{-1}) compared to the analogous fall of the ΔE_H term, and the resulting $\delta \Delta E_{p\text{-OH}}$ energies tend to be more positive. The same trend can also be expected in the considerations of other cases where carboxylic and phenolic groups ionize in aromatic molecules. The most simple example is the isodesmic process

$$C_6H_5OH + C_6H_5COO^{(-)} \rightleftharpoons C_6H_5O^{(-)} + C_6H_5COOH, \qquad (C)$$
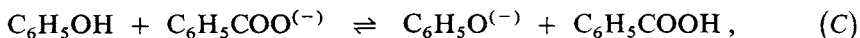
where the sign of the corresponding energy change

$$\delta \Delta E_{OH} = \Delta E_{OH} - \Delta E_H \qquad (3)$$

shows the relative gas phase proton affinities of phenol and benzoic acid (I).

If the simple STO-3G calculation of the particles C_6H_5OH and $C_6H_5O^{(-)}$ is performed in the same way as in the cases I through V, the energy values $E_{SCF} = -301·723573$ and $-300·974628$ ($E_{SCF} = E_{tot}/k$, where $k = 2\,625·5$ kJ mol^{-1}) are obtained in accordance with analogous published[8] calculations and hence, also with the theoretical energy of ionization $\Delta E_{OH} = -1\,966·36$ kJ mol^{-1}. Thus the total energy of the process (C) is $\delta \Delta E_{OH} = +4·9$ kJ mol^{-1} and reflects a slightly higher proton affinity of the C_6H_5COOH molecule as compared with that of the C_6H_5OH molecule. In accordance with the above-discussed findings concerning the influence of diffuse functions on the calculated SCF energy, the decrease expected for the "monooxygen" term ΔE_{OH} in Eq. (3) will not in any case be larger than that of the "dioxygen" term ΔE_H (446 kJ mol^{-1}) and also will not be higher than that of the analogous $\Delta E_{p\text{-OH}}$ term of the process (B), i.e. <340 kJ mol^{-1}. Consequently, it can be concluded that any extension of the AO basis set as well as its augmentation

with diffuse functions within the non-empirical MO treatment will always lead to more positive $\delta \Delta E_{OH}$ values than those obtained from the simple STO-3G basis set. Hence, the prediction based on the last above-mentioned simple approach already appears to be qualitatively correct, and the equilibrium (C) ought to be always shifted to the left at not too high temperatures.

The results presented show that the earlier theoretical presumptions[1,2] concerning the preferred mechanism of the gas phase dissociation of acid II according to scheme (B) do not seem to be justified, and so there is no reason to neglect the predominance of process (A). The previous non-empirical STO-3G treatments[2,9] proved to be insufficient for calculations of realistic $\delta \Delta E_{p\text{-}OH}$ energies owing to the comparatively large amount of only partially delocalized electron lone pairs in particles II, IV, and V. An argument in favour of the dissociation mechanism (B) is based on the observation[1] that there exist the same trends in changes of the Gibbs energies ΔG_X and the Hammett σ_X parameters, except for the case of $X = p\text{-}OH$. In our opinion, this correlation between both quantities is much too rough. If the parameters σ_X valid for solutions were also chosen for the gas phase measurements, then more positive values $(+0\cdot1$ to $+0\cdot2)$ would have to be taken for the $\sigma_{p\text{-}OH}$ parameter. We presume, however, that it would be more adequate to choose a completely new, quite different set of substituent parameters for gas phase processes.

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