April, 1991] © *1991 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 64, 1445—1446 (1991)* 1445

Comments on the "Synthesis and Characterization of Some New Organophosphonates and Their Adducts with Some Metals" by Saad and Ramadan[1)]

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Synopsis. This NOTE criticized experimental work, calculations and the conclusions based on them, in a paper recently publishied.[1)]

In the above paper the authors claim to have synthesized ethyl hydrogen benzoylphosphonate and ethyl hydrogen butyrylphosphonate by hydrolyzing the corresponding diethyl esters by sodium hydroxide. They claim to have obtained the compounds, although they describe neither their appearance and criteria for their purity nor analytical results, except for ionization constants and selected infrared data.

The authors of the paper cited above are apparently unaware of the long known fact that dialkyl acylphosphonates are sensitive to alkaline conditions,[2–5)] and hydrolyze rapidly to the corresponding carboxylic acids and to dialkyl phosphonate. Thus diethyl benzoylphosphonate and diethyl butyrylphosphonate certainly have undergone hydrolysis to benzoic or butyric acid and to diethyl (and/or ethyl hydrogen) phosphonate under the forcing conditions used by Saad and Ramadan (heating at 80 °C with a 6-fold molar excess of sodium hydroxide for 5 h in a sealed flask). This assumption is supported by the fact that the related dimethyl acetylphosphonate has been shown to hydrolyze with a half life of seconds at pH 7 at room temperature.[6)] More detailed studies of the kinetics of the hydrolysis have also been reported.[7,8)] Acylphosphonates are generally sensitive towards bases. For instance primary amines readily cleave the C-P bond in acylphosphonates and yield carboxamides and dialkyl phosphonates.[9)]

Because of this sensitivity to hydrolytic conditions, the preparation of salts of unesterified acylphosphonic acids requires the use of silyl halide dealkylation.[10)] Similarly, the preparation of salts of alkyl hydrogen acylphosphonate requires the use of a nonhydrolytic method, namely nucleophilic dealkylation by halides.[11)]

We were the first to isolate and to characterize acylphosphonic acids and the corresponding monoesters.[12)] Comparison of the infrared carbonyl frequencies reported by Saad and Ramadan for ethyl hydrogen benzoylphosphonate (1718 cm^{-1}) and ethyl hydrogen butyrylphosphonate (1740 cm^{-1}) with those reported by us for methyl hydrogen benzoylphosphonate (1650 cm^{-1}) and alkanoylphosphonates (1690 cm^{-1}) suggests that Saad and Ramadan had indeed benzoic acid and butyric acid, and not the compounds they claim, in their hand.

It is unfortunate that Saad and Ramadan did not make an effort to purify their hydrolysis products and seek proof of purity such as elemental analysis or homogeneity by chromatographic techniques. There is no doubt that the correct structures of the products would have become apparent if such efforts would have been made or if the products would have been examined by ^{31}P nuclear magnetic resonance spectroscopy.

The authors used the HMO method to correlate

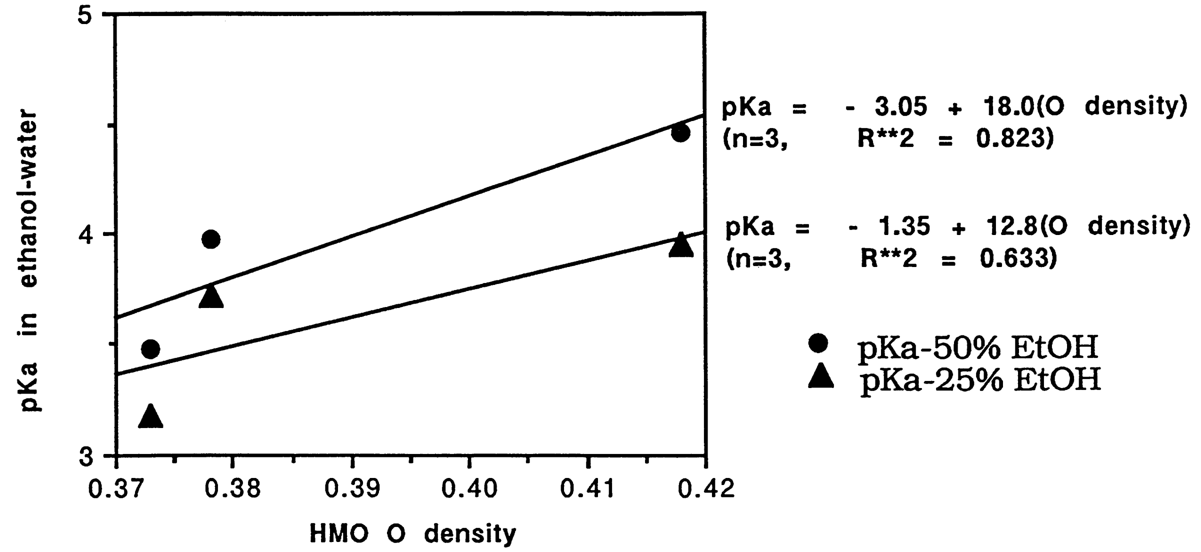

Fig. 1. pK_a dependence on oxygen densities, as reported by Saad and Ramadan.[1)] The equations and correlations are marked on the right hand side for each of the two lines, for 50% and 25% ethanol-water.

between measured pK_a values and electron density on the hydroxylic oxygen in these compounds. We would like to comment on the use of Hückel calculations by the authors as well as on their claim of existing correlation.

The reference for HMO cited by the authors[13] does not list any parameters for phosphorus, and the paper does not indicate which parameters were employed for α and for β of this element. In addition, it is clear, and also established by X-ray data (e.g. for sodium hydrogen acetylphosphonate[14]), that the phosphonate group is not planar. In such cases nonplanarity should be taken into account by variation of the value of β for the relevant atoms according to their angular deviation from planarity.[13] This is not mentioned as the procedure which was followed.

pK_a values represent a difference in stability between the neutral and deprotonated molecules in the current environment. Such an environment effect is reflected also in the experimental differences found by the authors between 50% and 25% ethanol-water mixtures. It is possible, in the framework of HMO,[13] to study such differences between neutral molecules and their anions. Unfortunately, the authors do not appear to have tested this option.

The authors further claim that the decrease in electron densities of the hydroxylic oxygen in the three compounds "··· is consistent with the order of increasing acidity and accounts for the closest pK_a values of the butanoyl and benzoyl derivatives, 3.98 and 3.48, respectively". However, the correlation coefficient for the three compounds is very poor with $R^2=0.823$, for these pK_a values in 50% ethanol-water. The correlation for the 25% ethanol-water is even poorer, with $R^2=0.633$. Figure 1 clarifies this point.

A final point concerns the values of electron densities obtained by the authors. The overall density on the phenyl ring of the benzyl derivative is 5.272 (out of the original 6 electrons). In the benzoyl derivative, it is 5.610. This indicates that with their calculations, the authors find that a carbonyl adjacent to a phenyl ring is donating electrons to the ring, compared to a methylene at the same position, all other things being equal. This result should have made clear to the authors that something is wrong with the results, with the method or with their scheme of parametrization.

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