

Different Surface Activity of Quaternary Ammonium and Phosphonium Ions in Formamide Solutions

Fredrik Bökman,^a Ove Bohman^a and Hans O. G. Siegbahn^b

^aDepartment of Organic Chemistry, Box 531, University of Uppsala, S-751 21 Uppsala, Sweden and ^bDepartment of Physics, Box 530, University of Uppsala, S-751 27 Uppsala, Sweden

Bökman, F., Bohman, O. and Siegbahn, H. O. G., 1992. Different Surface Activity of Quaternary Ammonium and Phosphonium Ions in Formamide Solutions. – *Acta Chem. Scand.* 46: 403–405.

Tetrabutylammonium and tetrabutylphosphonium ions are often used in synthetic applications as phase-transfer catalysts.¹ The influence of the type of catalyst on reactions has been the subject of many investigations e.g. concerning the kinetics of etherification reactions, where the distribution of different quaternary catalyst ions between the two phases is discussed.² An important aspect of the phase-transfer system is the surface-active behaviour of the catalyst at the interface between the two media. It is not always clear to what extent this aspect will be rate-determining for a particular catalytic process or whether the reaction in the organic phase is the important step. In a recent paper³ dealing with this issue a comparison between reaction rates for catalysts with different quaternary chain lengths showed that the catalysts with the greatest ability to reduce the interfacial tension lead to the highest reaction rates. In order to shed further light on these matters it thus seems appropriate to investigate further interfacial aspects in these systems. Information obtained concerning the aqueous phase-vacuum interface is also highly relevant here since the cation-anion interaction on the aqueous side, largely responsible for the surface segregation, will, to a large extent, be expected to be independent of the nature of the adjacent medium.

Results and discussion

In this communication we report results obtained using electron spectroscopy to investigate solution-vacuum interfaces. Owing to its surface sensitivity, electron spectroscopy has been found to yield valuable information on ion distributions between bulk and surface.⁴ We have previously reported on studies of tetraalkylammonium ions in formamide solutions.⁵⁻⁷ In these studies depth profiles of the ions were investigated in terms of their dependence on cation and anion type. Surface excess was found to depend on cation hydrocarbon-chain length and different anion-cation distributions were observed depending on the anion identity. The latter results were interpreted as being due to the formation of contact ion pairs at the surface for some of the anions investigated. In a recent study⁸ salting-out ef-

fects have been observed on addition of ammonium chloride to solutions of quaternary ammonium bromide. It was found that the chloride and the bromide ions both take part in the surface layer as counterions to the positively charged overlayer.

The results presented here pertain to tetrabutylammonium and tetrabutylphosphonium bromides in formamide solution. Formamide may be considered sufficiently aqueous-like also to render our results qualitatively valid for water solutions,⁹ and in fact, the results that we have obtained so far on these systems support this assumption.⁵⁻⁸ Formamide is a suitable solvent for electron spectroscopic studies because of its low vapour pressure.

Spectra were recorded as a function of take-off angle of the photoelectrons with respect to the solution surface. This means that the surface sensitivity can be varied continuously with the highest sensitivity at low angles. Fig. 1

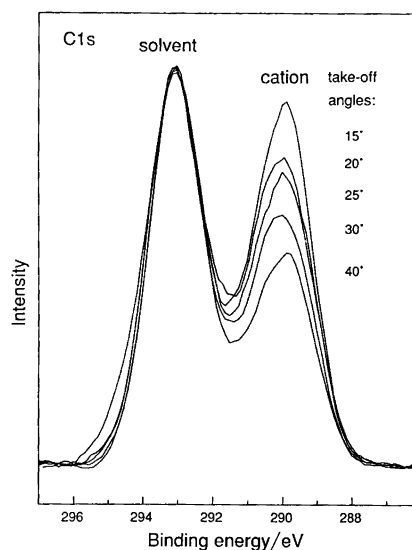


Fig. 1. C1s spectra of a 0.5 m solution of tetrabutylammonium bromide in formamide recorded at different take-off angles of the photoelectrons with respect to the solution surface. The spectra are normalized to the solvent peak and peak height. The intensity is in arb. units.

shows C1s spectra obtained from a 0.5 *m* solution of tetrabutylammonium bromide in formamide at different angles. The signals due to the solvent and the solute cation appear as two well resolved peaks and the spectra are normalized to the former peak. As can be seen, the solute peak increases substantially with respect to the solvent peak with decreasing take-off angle. In Table 1 the relative intensity numbers obtained for the different angles are displayed (note that the solute peak is somewhat wider). These numbers are all seen to be much larger than the ratio expected from the bulk stoichiometry (0.36). These findings clearly show that the tetrabutylammonium ions form an overlayer on the solution surface. If a correction is made for the bulk contribution the numbers in Table 1 can be used together with known values for the photoelectron mean free path to calculate the surface coverage of cations on the surface.¹⁰ In this case one finds a value of 5.6×10^{17} cations m^{-2} which together with an estimated diameter for each ion of ca. 10 \AA gives a surface coverage of approximately 40% of a monolayer. Earlier results on quaternary ammonium bromides indicate that the cations in this case probably form contact ion pairs with the anions.⁵⁻⁸

Considering next the tetrabutylphosphonium bromide solution, Fig. 2 shows the corresponding C1s spectra and Table 1 the relative intensity numbers. The angular variation of the intensities is seen to have the same qualitative behaviour as for the ammonium analogue, but the values are significantly different. The conclusion from the figures is that the phosphonium compound is substantially more surface active. A corresponding calculation of surface coverage yields a value of about 80% of a monolayer in this case (again assuming an ionic size of ca. 10 \AA). The large effect found is surprising and indicates the importance of specific interactions when deciding the surface activity in these systems. A difference in the surface structure between phosphonium and ammonium analogues in solution has not, to our knowledge, been previously noted. This finding may have implications on the possible influence of interfacial behaviour in phase-transfer catalysis.

An important practical aspect from a preparative chemical viewpoint using onium salts is the higher thermal stability of the phosphonium salts compared with ammonium

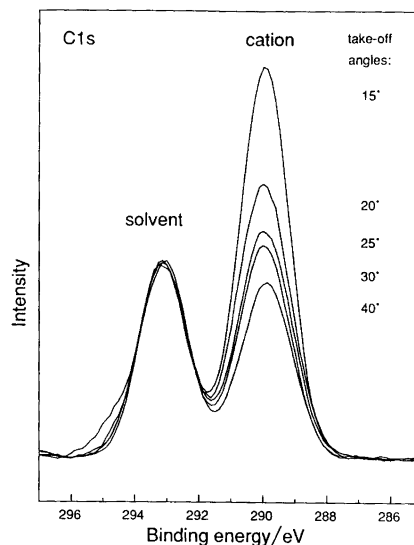


Fig. 2. C1s spectra of a 0.5 *m* solution of tetrabutylphosphonium bromide in formamide recorded at different take-off angles of the photoelectrons with respect to the solution surface. The spectra are normalized to the solvent peak and peak height. The intensity is in arb. units.

salts. However, studies of nucleophilic reactivity in organic solvents¹¹ show that tetraalkylammonium bromide salts are considerably more reactive than analogous phosphonium salts. These kinetic results and the surface-segregation results presented here can both be explained as effects of a strong attractive interaction between the phosphonium ion and bromide ion. The strength of this interaction, compared with the corresponding interaction for the ammonium ion, can be due either to the longer carbon-heteroatom bond, making the positive charge more accessible, or to the larger polarizability of phosphorus compared with nitrogen, or a combination thereof.

Table 1 also gives the ratio between the P2p and Br3d peaks at take-off angles of 40° and 20°. When corrected for the difference in photoelectric cross-section,¹² these measured intensity ratios imply a cation-to-anion ratio at the surface of close to 1. This finding, together with the observation that the measured ratios do not depend on take-off angle, is strong evidence for contact ion pairing at the surface.

Experimental

The experimental arrangements for obtaining electron spectra from solutions are described in more detail elsewhere.⁴⁻⁷ Chemicals used were of commercial grade.

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Table 1. Quaternary ammonium and phosphonium bromide 0.5 *m* in formamide. Bulk ratio C1s(cation)/C1s(solvent) = 0.36.

Take-off angle	Peak intensity ratios		
	$(C_4H_9)_4N^+Br^-$		P2p(cation)/ Br3d(anion)
	C1s(cation)/ C1s(solvent)	C1s(cation)/ C1s(solvent)	
40°	0.70	0.96	0.504
30°	0.85	1.15	—
25°	0.98	1.30	—
20°	1.00	1.62	0.519
15°	1.28	2.21	—

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Received September 11, 1991.