Interaction of Ions with Carbonyl Donors: ^{13}C and ^{23}Na Nuclear Magnetic Resonance Spectra

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The ^{13}C n.m.r. spectra of a few carbonyl donors have been recorded in the presence of Li^+, Na^+, and Mg^{2+}. The ^{13}C resonances of carbonyl and other groups shift downfield on interaction with the ions. The solvation numbers of Na^+ with acetone and cyclohexanone have been determined from ^{23}Na n.m.r. spectra.

In recent years, spectroscopic methods have been increasingly used to investigate the nature of ion–molecule interactions.[1–3] Popov and his co-workers [4–7] have made extensive contributions to the study of ion–molecule interactions by monitoring cation resonances (*e.g.* ^7Li, ^{23}Na, ^{133}Cs, *etc.*) in the n.m.r. spectra of solutions. However, there have been very few investigations on the effect of cations on the ^1H or ^{13}C resonance spectra of molecules. In spite of the low abundance of the ^{13}C isotope, chemical shifts have provided useful information in some cases.[8–10] Adams and his co-workers [8] have studied the effect of Li^+ on the ^{13}C spectra of dimethylacetamide in aqueous solution. Rao and his co-workers [9] have examined the interaction of Li^+, Na^+, Ba^{2+}, Ca^{2+}, and Mg^{2+} with dimethylformamide and dimethylacetamide by measuring the effect of the ions on ^{13}C chemical shifts.

Although it is qualitatively known that ions interact with the oxygen atom of a carbonyl group, systematic data are not available on the interaction of alkali and alkaline earth metal salts with simple carbonyl compounds. Of special interest is the effect of such an interaction on other carbon atoms. Therefore, the interaction of Li^+, Na^+, and Mg^{2+} with simple carbonyl compounds has been examined by ^{13}C n.m.r. spectroscopy. Also, the ^{23}Na n.m.r. spectra of sodium tetraphenylborate in the presence of a few ketones have been obtained.

Experimental

The ketones and the solvent nitromethane (B.D.H.) were dried and purified by fractional distillation. The salts $LiClO_4$, $NaClO_4$, and $Mg(ClO_4)_2$ were of AnalaR grade and were dried by keeping *in vacuo* above 100 °C and at 4—10 Torr pressure for 2—3 days. Sodium tetraphenylborate (B.D.H.) was dried at room temperature under vacuum without further purification. All the salts were stored in a vacuum desiccator. Doubly distilled water was used and fresh solutions were prepared just before the start of the experiment. Precautions were taken for minimum exposure of salts and solutions to air.

The ^{13}C and ^{23}Na chemical shifts were determined using a JEOL FX 100 multinuclei Fourier transform n.m.r. spectrometer with a magnetic field of 2.3 T operating at 24.99 and 26.29 MHz, respectively, at 27 °C. The spectra were obtained in 10 mm spinning sample tubes with a 1 mm inner tube containing Me_4Si and D_2O to provide the deuterium lock and the external chemical shift standard. The ^{13}C chemical shifts were measured with reference to Me_4Si. The ^{23}Na chemical shifts were obtained with reference to 1.0 mol dm^{-3} NaCl in water as external reference. No correction was made for bulk diamagnetic susceptibility effects, as they are expected to be small and do not affect the overall conclusions which are based on the measurement of relative shifts. A downfield shift from the reference is considered positive. This convention is in accord with that of Smetana and Popov.[6]

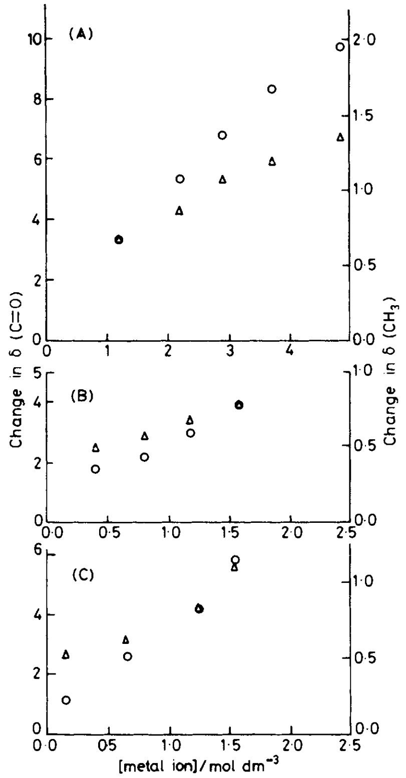


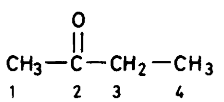
Figure 1. Effect of metal perchlorates on ^{13}C chemical shifts of acetone (neat liquid): ○, C=O; △, CH_3. (A) Li^+, (B) Na^+, (C) Mg^{2+}

Results and Discussion

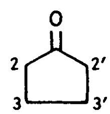
^{13}C *N.m.r. Spectra.*—The effect of increasing concentrations of $LiClO_4$, $NaClO_4$, and $Mg(ClO_4)_2$ on the ^{13}C chemical shifts of neat (pure) acetone, butan-2-one, mesityl oxide, cyclopentanone, and cyclohexanone have been studied and the results for acetone (^{13}C=O and $^{13}CH_3$) are shown in Figure 1. Typical data on the effect of lithium, sodium, and magnesium perchlorates on the various carbon atom resonances of butan-2-one are shown in the Table. The ^{13}C resonances of all ketones are shifted downfield with an increase in the concentration of ion. The effect on the carbonyl ^{13}C resonance is much greater than that on other carbon resonances. This indicates that metal ions bind to the carbonyl oxygen, thereby reducing the electron density at carbonyl carbon to a greater extent. The electron density at the other carbon atoms is affected to a smaller extent. The carbonyl carbon atoms in neat cyclopentanone and cyclohexanone are more deshielded than those of acyclic ketones. The $\delta_{C=O}$ value of cyclopentanone is

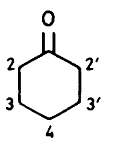
Table. Effect of metal ions on the ^{13}C chemical shifts δ of butan-2-one (neat)

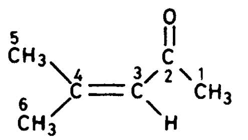
Concn. of salt (mol dm^{-3})	δ (p.p.m.) C-1	C-2	C-3	C-4
LiClO$_4$				
	28.9	207.6	36.4	7.6
0.43	29.0	208.8	36.5	7.7
0.97	29.1	209.7	36.6	7.7
1.19	29.2	210.1	36.7	7.8
1.62	29.4	211.8	36.9	7.9
2.16	29.4	212.7	37.0	7.9
NaClO$_4$				
0.33	29.0	208.5	36.5	7.7
0.66	29.2	209.4	36.6	7.8
0.99	29.2	210.1	36.7	7.8
1.32	29.3	210.2	36.8	7.8
Mg(ClO$_4$)$_2$				
0.30	29.1	209.0	36.6	7.8
0.46	29.2	202.2	36.7	7.8
0.61	29.3	210.4	36.8	7.9
0.92	29.4	210.9	36.9	8.0



$$\underset{1}{CH_3}-\underset{2}{\overset{\overset{O}{\|}}{C}}-\underset{3}{CH_2}-\underset{4}{CH_3}$$







larger (more deshielded) than that of cyclohexanone mainly due to electronic rather than strain effects.[11] C-2 and -2′ of cyclopentanone are also much more deshielded than C-3 and -3′. The interaction of metal ions with cyclopentanone results in more deshielding of the carbonyl carbon resonance as well as that of C-2, -2′, -3, and -3′. In the interaction with ions with cyclohexanone, appreciable deshielding of the carbonyl carbon resonance occurs, but the resonances of C-2, -2′, -3, and -3′ are not significantly affected compared with C-4; this carbon atom is in fact shielded.

The effect of metal ions on the ^{13}C spectra of mesityl oxide is interesting. Based on the known ^{13}C n.m.r. spectra of cyclohexenone,[12] the carbonyl and ethylene carbon atom (C-3 and -4) resonances have been assigned chemical shifts of δ 197.05, 124.58, and 153.95 respectively. On interaction with metal ions, the $\delta_{C=O}$ is shifted to high values. The shifts of ethylene carbon atoms are less compared with those of the carbonyl carbon. Therefore, the interaction predominantly occurs at the carbonyl oxygen. The changes in chemical shifts of C-3 and -4 may possibly indicate that the ion interacts with the π electron cloud of the ethylene group as well. The changes may even be due to simple conjugation effects.

The changes in $^{13}C{=}O$ chemical shifts due to the interaction with Li$^+$, Na$^+$, and Mg^{2+} ions are plotted against the ionic potential (charge/ionic radius) of these ions. The plot (Figure 2) is approximately linear. Similar linear relationships have been observed for other carbon atoms.

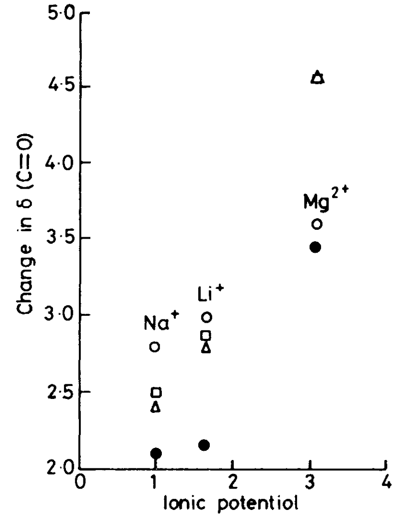


Figure 2. Effect of ionic potential (charge/ionic radius) of cations on $^{13}C{=}O$ chemical shifts of various ketones (neat liquids): ○ acetone, △ cyclohexanone, □ cyclopentanone, ● mesityl oxide

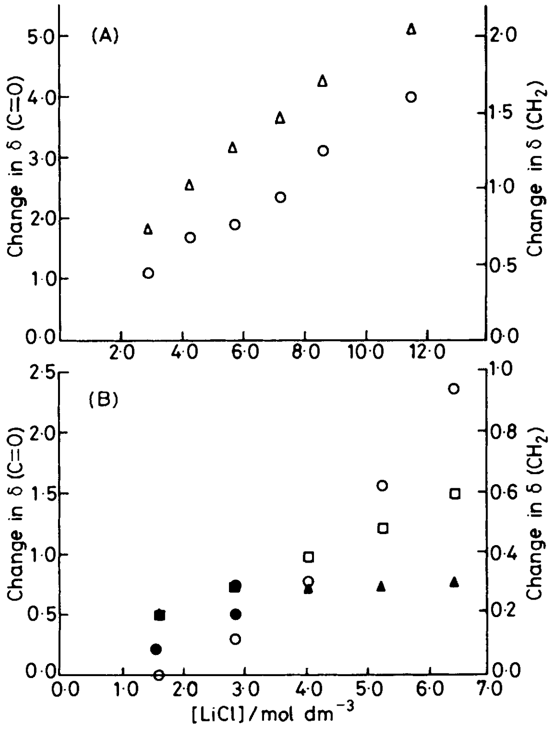


Figure 3. Effect of LiCl on the ^{13}C chemical shifts of (A) acetone in aqueous medium and (B) cyclohexanone in 50% (v/v) aqueous methanol: (A) ○, C=O; △, CH$_3$. (B) ○, C=O; □, C-2; ●, C-3; and △, C-4

We next examined the effect of ions on ^{13}C resonances of a few ketones in aqueous solution. Where the solubility of ketones in water is not appreciable, 50% H_2O–50% methanol was employed. Thus, the ^{13}C spectra of cyclopentanone and cyclohexanone in the presence of LiCl have been recorded in this solvent mixture. The effect of LiCl in aqueous solution or water–methanol is to cause downfield shifts of all the carbon

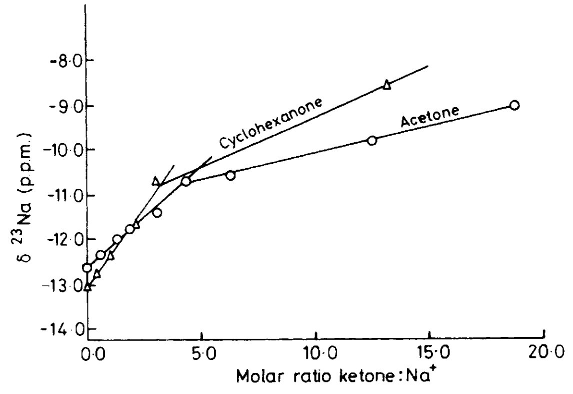


Figure 4. Sodium-23 chemical shifts as a function of the ketone: Na^+ mol ratio in nitromethane

atoms, similar to those in neat liquids. Typical results on the influence of LiCl on ^{13}C chemical shifts of acetone and cyclohexanone are shown in Figure 3. Since the trends in shifts upon addition of LiCl are similar to those of perchlorate salts in neat ketones, no attempt was made to measure the shifts as a function of the composition of the solvent mixture. The effects of variation of solvent composition on chemical shifts is expected to be minimal as water and methanol solvate the ions to the same extent. Similar observations have been made for dimethylacetamide [8,9] and dimethylformamide.[9] The $\Delta\delta$ values in aqueous solution are, however, smaller than in neat liquid. A comparison of carbonyl chemical shifts of aqueous LiCl solutions of acetone with $LiClO_4$ solutions in neat acetone show that the shift observed at the highest salt concentration in aqueous solution (*ca.* 11.5 mol dm^{-3} LiCl) corresponds to that obtained with a *ca.* 1.5 mol dm^{-3} solution of $LiClO_4$ in neat acetone. This is possibly due to extensive solvation of Li^+ and Cl^- ions in aqueous solution, which decreases the availability of Li^+ for direct binding with carbonyl oxygen. Further, the strong hydrogen bond formation between water and carbonyl oxygen will also hinder the interaction of Li^+ with the carbonyl group.

^{23}Na *N.m.r. Spectra.*—In view of the results obtained from ^{13}C n.m.r. spectra on the interaction of cyclic and acyclic ketones with Li^+, Na^+, and Mg^{2+}, it was considered interesting to monitor ^{23}Na resonance in the presence of a few carbonyl donors. Therefore, the variation of ^{23}Na chemical shifts of sodium tetraphenylborate in nitromethane at several concentrations of acetone and cyclohexanone were determined. It was noticed that with an increase in concentration of acetone or cyclohexanone, deshielding of ^{23}Na nucleus occurs resulting in a downfield shift.[13] The ^{23}Na chemical shifts have also been determined as a function of ketone–metal ion mol ratio and the results for interaction of Na^+ with acetone and cyclohexanone are shown in Figure 4. Similar plots have been obtained by Wuepper and Popov for the solvation number of Na^+ with DMSO[14] and a few crown ethers.[5] It can be seen from Figure 4 that the solvation number for the interaction of Na^+ with acetone is four and that with cyclohexanone three. The lower solvation number of sodium ion with cyclohexanone is possibly due to a steric effect.

Acknowledgements

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