Short Communications

A working hypothesis for negative ion generators

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Summary. The effects of negative ion generators may be explained by reactions of carbonate radical anion, or alternatively, by physical factors such as the electric field of the ions generated by these apparatuses.

Atmospheric electricity and the influence of gaseous ions on the well-being of humans have been topics of continuous interest in biometeorology[1-5]. Particularly the suggested correlation between the ill effects of so-called 'evil winds' such as the hot, dry, Khamsin (Sharav) in the Middle East or the Foehn in Central Europe, and the ratio between atmospheric negative and positive ions has attracted attention[6,7]. Sulman softened these kind of effects with artificially-generated negative air ions (AGNI)[8-10]. His group also reported that these ions affect the frequency of the alpha-waves as monitored by EEG[11]. Research on the biological effects of AGNI has recently revived after an initial setback due to FDA regulations in the mid-1950's[5]. Simultaneously due to the increasing public concern with the indoor pollution, the air ionizers industry seems to be recovering[12].

This report assesses from a physico-chemical point of view modern negative ion generators. The evidence to substantiate the various claims of AGNI has been severely handicapped by a very limited understanding of the factors involved. Until recently, no chemical definition for 'negative air ions' had been suggested, and consequently no investigation of the interaction between well-defined ionized air species and biological molecules were carried out.

The modern negative ion generators are of the corona discharge type. Some have fans and dust filters; some do not. It is noted that this apparatus is not to be confused with electronic air cleaners which are installed in the air duct of air conditioned homes and are optimized electrostatic filters for household use.

The exact nature of the negative air ions generated in this way, with one notable exception[13], has never been defined by the adepts of air ionization. However, the negative ion species generated in the air by corona discharge have been identified accurately by mass spectrometry[14]. At atmospheric pressure, in static or dynamic conditions, carbonate radical anion, $CO_3^{\overline{\cdot}}$, is the dominant species produced. These ions were found to be due to small concentrations of CO_2 in air. CO_2 apparently reacts with O^- or $O_3^{\overline{\cdot}}$ to form $CO_3^{\overline{\cdot}}$. It was estimated that only about 40 ppm of CO_2 is needed at atmospheric pressure to convert all oxygen atoms to $CO_3^{\overline{\cdot}}$ species. The carbonate radical anion can also be readily generated very efficiently in aqueous solution[15]. It can be produced by oxidation of carbonate or bicarbonate with OH or $SO_4^{\overline{\cdot}}$ radicals (Eq. 1,2)

$$CO_3^{2-} + OH^{\cdot} \rightarrow CO_3^{\overline{\cdot}} + OH^- \qquad (1)$$

$$CO_3^{2-} + SO_4^{\overline{\cdot}} \rightarrow CO_3^{\overline{\cdot}} + SO_4^{2-} \qquad (2)$$

by photoionization of carbonate (Eq. 3)

$$CO_3^{2-} + h\nu \rightarrow CO_3^{\overline{\cdot}} + e_{aq}^- \qquad (3)$$

or by photolyses of certain carbonate-metal complexes (Eq. 4)

$$Co(NH_3)_4CO_3^+ + h\nu \rightarrow CO_3^{\overline{\cdot}} + Co^{2+} + 4NH_3 \qquad (4)$$

Subsequently, its reaction with a broad range of chemical compounds has been investigated and the reaction rates determined very accurately. The general reaction pattern resulting from these studies indicate that carbonate radical can oxidize certain aromatic and heterocyclic compounds and inorganic ions, probably by direct electron transfer. It can also abstract hydrogen atom from aliphatic compounds but this reaction is generally slow. Thus the reaction with aliphatic amino acids or pyrimidine bases proceeds with a reaction rate $k < 10^4\ M^{-1}sec^{-1}$ while aromatic amino acids such as tryptophan, tyrosine or sulfur-containing amino acids like cysteine and methionine react with $k > 10^8\ M^{-1}sec^{-1}$. In spite of this extensive available data, the possible involvement of $CO_3^{\overline{\cdot}}$ in biological effects of AGNI has never been considered by the promoters of the air ionization. On the contrary, in 1979 Kellogg et al.[13] postulated the involvement of superoxide radical anion $O_2^{\overline{\cdot}}$, in the bactericidal effects of AGNI. This conclusion was based on the observation that the enzyme superoxide dismutase completely protected bacteria in aqueous suspension against killing by air ionization. This enzyme is known to remove $O_2^{\overline{\cdot}}$ efficiently by catalyzing its disproportionation into H_2O_2 and molecular O_2. Obviously, regardless of the identity of negative ions in air, it is possible that upon addition to aqueous solution, they are transformed to $O_2^{\overline{\cdot}}$. However, this reaction is hardly plausible since the carbonate radical reacts with $O_2^{\overline{\cdot}}$ with a very rapid rate of $1.5 \times 10^9\ M^{-1}sec^{-1}$ (Eq. 5)[15].

$$CO_3^{\overline{\cdot}} + O_2^{\overline{\cdot}} \rightarrow CO_3^{2-} + O_2 \qquad (5)$$

In addition to this suggested involvement of $CO_3^{\overline{\cdot}}$ in underlying chemical reactions which might explain the biological effects, we revive the hypothesis that at least the bactericidal effect of AGNI could be explained by cell agglutination in the electric field of the ions produced by ion generator[16,17]. As already mentioned, the working principle of the ion generators is the corona discharge. The corona is formed when the instrument is energized at a high enough voltage to induce the ionization of the gas around the discharge electrode.

In negative polarity corona, the positively charged ions are attached to the discharge electrode and are neutralized. The electrons move to the region of the lower potential where they attach to gas molecules, transforming them into gas ions, and thus creating a spacial electric field. The gas ions travel through the space and can become attached, or transfer the charge, to other particles via several processes such as: field-directed charging, ion-diffusion charging, on direct-electron attachment, thus converting them into charged particles. This electric field becomes oriented if grounding is provided. The grounding can be accidental, for example, through the walls of the chamber, or intentional through a grounded solution exposed to the air ions. In the latter case the gas ions could become attached to particles in solutions such as microorganism cells. Both the particle charge and the electric field gradient set up forces causing the particle to migrate. The particle movement is a function of particle size, its overall net charge and the field strength. This movement, and the subsequent collosions, can lead to the agglutination of the cells.

This possibility was discussed and rebutted previously by Krueger's group[18] on the following grounds: a) the lethal effect of bacterial cells was reversed by exposing the cells 'to intense light in the visible spectrum' and b) 'the time required to produce a lethal effect was much less than the minimal time for agglutination predicted by Smoluchowski equation'. We are unable to estimate the relevance of the first claim since no pertinent data such as conditions of irradiation, extent of reversal etc. were provided. Furthermore, we consider that the application of the Smoluchowski equation[19] for agglutination due to an external electric field is entirely irrelevant. This equation refers to Brownian motion and does not make any provision for an external factor.

Recently the same group emphasized, as crucial, the necessity of grounding and stirring the solutions exposed to AGNI. This requirement is supposed to ensure adequate contact of ions and cells at the air-water surface and to avoid conditions of minimal negative ion interaction, as accumulated surface charge would repel negative ions[20]. We find this explanation hardly acceptable because the target solutuion is an electrolyte with a good conductivity which cannot accumulate surface changes. If grounding is necessary, it is for creating an effective electric field.

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Indirect ligand attachment to metal centers via hydrogen bonding to coordinated water molecules

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Summary. The 1:1 complex between triphenyltin chloride and **I** has a structure involving the indirect attachment of the ligand to the metal center, via hydrogen-bonding to a coordinated water molecule.

Coordinated water molecules can hydrogen bond to planar tridentate chelating agents and hold them in close proximity to a tin (IV) metal ion center.

We describe the synthesis of a series of organotin complexes which contain coordinated water molecules displaying a hitherto unreported type of bridging behavior.

The planar tridentate chelating agents 2,2′:6′,2″-terpyridyl and 3-(2-(1,10-phenanthrolyl))-5,6-diphenyl-1,2,4-triazine (**I**)[2] form 1:1 complexes with triphenyltin chloride and triphenyltin isothiocyanate[3].

Crystallographic data

Compound	Lattice	Space group	Cell dimensions		Final R_f-value
$Ph_3SnNCS \cdot terpy \cdot H_2O$	Triclinic	$P\bar{1}$	a = 10.326 Å b = 10.739 Å c = 15.880 Å	$\alpha = 105.04°$ $\beta = 97.14°$ $\gamma = 111.5°$	0.026
$Ph_3SnCl \cdot L \cdot H_2O$ (L = I)	Orthorhombic	$Pca2_1$	a = 19.195 Å b = 9.144 Å c = 21.642 Å	$\alpha = 90°$ $\beta = 90°$ $\gamma = 90°$	0.029