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THE IONIZATION POTENTIALS OF BIOLOGICAL PURINES AND PYRIMIDINES

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The possibility has often been discussed(1) that purines and pyrimidines may form charge-transfer complexes with various organic compounds and that such complexes may play a role in the biological activity of these compounds. These complexes are formed by a partial transfer of an electron from the highest filled molecular orbital of the "donor" to the lowest empty molecular orbital of the "acceptor"(2) and it is well known that these two energies are related to the ionization potential I_D of the donor and the electron affinity E_A of the acceptor. Very few experimental data are available on the ionization potentials of biological compounds in general(3) and of purines and pyrimidines in particular (and even fewer on their electron affinities). Purines and pyrimidines are expected to behave in charge transfer complexes rather as electron donors than as acceptors(1), a situation which makes the knowledge of their ionization potentials particularly useful. On the other hand if, as it seems now probable(4), the purines and pyrimidines are involved in a number of molecular complexes through the more classical Van der Waals-London interactions, this makes this knowledge still more useful because of the role of the ionization potential in the expression of the dispersion forces.

For the measurement of the ionization potentials we have used a mass spectrometer(5). The method is general with the one limitation that it cannot be applied to substances which are not volatile without decomposition. Orotic acid gave an initial molecular peak m/e = 112, which corresponds to its decarboxylation product, uracil.

The mass spectrometer used was an Atlas CH4 instrument (8 in. radius of curvature, 60° sector-field). An accelerating voltage of 3000 V, the TO 4 ion source (with gas cartridge) and magnetic scanning were employed. As temperatures of 150-250° were needed for the vaporization of the samples, a high temperature inlet system served to introduce the solid samples.

Simultaneously with the sample studied a rare gas (argon, krypton or xenon) was introduced into the ion source through the molecular flow inlet system of the instrument. The ionizing electron beam was "trap" current kept at 20 or 40 µ, whilst the nominal electron energy varied from 0 to 100 V in 0.1 V increments. Ion-currents were measured by means of an electron multiplier and a recording potentiometer.

The determination of the ionization potential was carried out as follows : the sample was vaporized and the intensity of the parent ion peak at 50 eV was recorded. Then the rare gas was introduced and the pressure adjusted until it showed an ion peak of similar intensity. The ionizing energy was varied in 0.1 eV increments in the region a few eV above the onset, and the intensity of the parent ion peak recorded again, both for the sample and the rare gas. The whole operation was repeated several times; in order to correct for eventual pressure changes, the intensity at 50 eV was recorded repeatedly at certain time intervals.

Then the logs of the ratios ion current I at a certain energy: ion current I_{50} at 50 eV were plotted against the nominal ionizing energies for the sample and the rare gas. These plots were practically all linear in the range $I : I_{50} = 10^{-4}$ to 10^{-2}, and the lines for the sample and the gas were parallel (method of Lossing (6)). Typical results for uracil and adenine are illustrated by Figures 1 and 2.

The ionization potentials of the compounds tested were computed from the known ionization potential of the rare gas used and the observed difference in the appearance potential of the sample and the rare gas. The results are summarized in Table I; the limits of error indicated in the Table take into account the spread of the experimental results in the different runs carried out with the same compound.

The experimental results are compared in Table I with theoretical values found by quantum-mechanical calculations using a highly refined semi-empirical self-consistent field method (7). The details of the procedure employed are indicated in ref. 7. It is remarkable that the sequence of the theoretical and experimental values is practically identical, although the numerical values of the two columns differ by an almost constant figure of 0.8 eV. It is intended to use the experimental results (the first of their type) in order to improve still more the calculations. It should be borne in mind that the "vertical" ionization potentials measured here may well be greater than the "adiabatic" potentials (6,8).

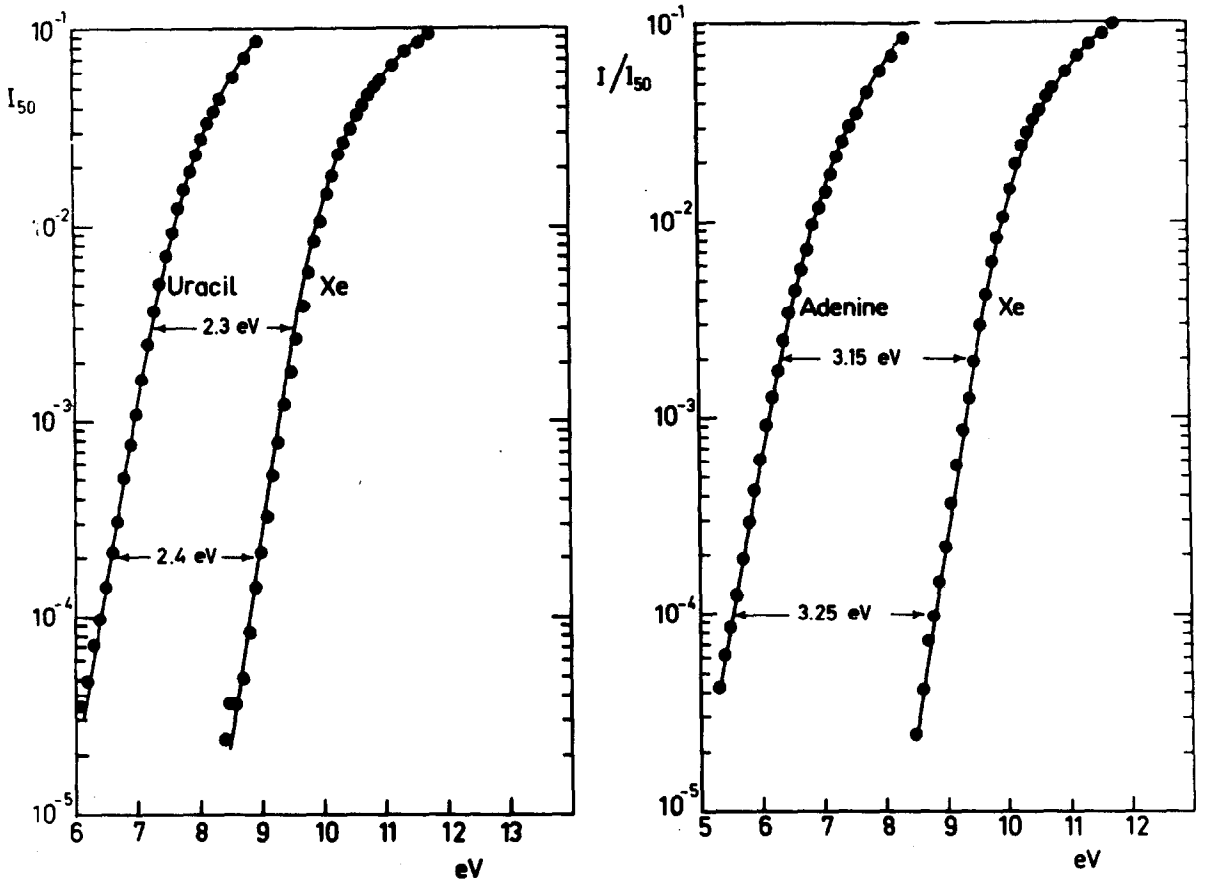

TABLE I

Compounds	Ionization Potential(in eV found	calculated
6-Azauracil	10.18±0.1	9.65
Uracil	9.82±0.1	9.15
Purine[a)]	9.68±0.1	8.87
Thymine	9.43±0.1	8.80
Xanthine	9.30±0.2	8.82
Hypoxanthine	9.17±0.1	8.00
Adenine	8.91±0.1	7.92
Cytosine	8.90±0.2	8.16
Tetramethyluric acid	7.87±0.1	≈ 7

[Note : a) The ionization potential of pyrimidine (9.91± 0.5 eV) has been determined by Omura (I. Omura, H. Baba and K. Higasi, Bull. Chem. Soc. Japan, 30, 633 (1957)] .

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