# Localised or Delocalised Charges in Molecule–Ions?

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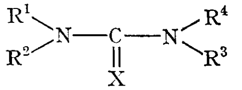
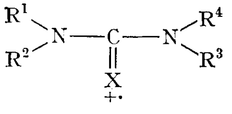
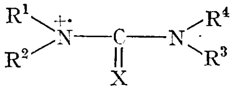
IN the course of a study of electron-impact fragmentation of systems of the type (I) we have recently published the ionisation potentials of the *N*-methylated thioureas.[1] We now communicate the corresponding results for the ureas, measured under the same conditions as described previously.


(I)

The results are shown in the Table, which also lists values for the systems $R^1R^2R^3N$, $R^1R^2O$, and $R^1R^2S$. As was pointed out previously, the small range of values for the thioureas as compared with either $R^1R^2R^3N$ or $R^1R^2S$ suggested that the effect of methylation was second order on the sulphur atom, and that the ground state of the molecular ion was probably better represented by (II) rather than (III).


(II)


(III)

The results reported for the ureas on the other hand are best interpreted as (III). In the first place, the range of values is much greater (1·53 ev) than for the thioureas (0·55 ev), indicating a first-order effect of methyl substitution. And secondly the order of the *NN*- and *NN'*-compounds is reversed in the ureas as compared with the thioureas. For a first-order effect, the result of *NN*-methylation should be appreciably greater than for *NN'*-methylation. The reverse is true for a second-order effect. This is in accord with the observations.

The detailed mass spectra will be discussed elsewhere. It suffices to say at present that while rearrangement peaks corresponding to the loss of $H\dot{S}$ or $H_2S$ arise from an important fragmentation route in the case of the thioureas, the loss of $\dot{O}H$ or $H_2O$ is relatively unimportant in the case of the ureas. The general conclusion to be drawn from this study is that localisation of the charge in certain molecular ions is not only a useful concept,[2] but one that can be justified by energetic considerations.

TABLE

| Compound | Ionisation potential (ev) | | | | |
|---|---|---|---|---|---|
| | Urea | Thiourea | $R^1R^2R^3N$† | $R^1R^2O$† | $R^1R^2S$† |
| Unsubstituted .. .. .. .. | 10·27 | 8·50 | 10·41 | 12·75 | 10·48 |
| Methyl .. .. .. .. .. | 9·73 | 8·29 | 9·47 | 10·91 | 9·44 |
| *NN*-Dimethyl .. .. .. .. | 9·10 | 8·34 | 9·21 | 10·1 | 8·73 |
| *NN'*-Dimethyl .. .. .. .. | 9·42 | 8·17 | — | — | — |
| Trimethyl .. .. .. .. .. | 8·94 | 7·93 | 8·60 | — | — |
| Tetramethyl .. .. .. .. | 8·74 | 7·95 | — | — | — |

†The ionisation potentials quoted represent an average of recent electron-impact values taken from the compilation of Kiser, "Tables of Ionisation Potentials" (TID-6142), University of Kansas, 1960, and the "Supplement", 1962.

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[1] M. Baldwin, A. Kirkien-Konasiewicz, A. Maccoll, and B. Saville, *Chem. and Ind.*, 1966, 286.

[2] F. W. McLafferty, *Chem. Comm.*, 1966, 78.