Charge Location and Fragmentation under Electron Impact

IV—The Behaviour under Electron Impact of some *N*-Methyl, *N'*-R-1,2,4-phosphadiazetidine-3-ones and Related Compounds

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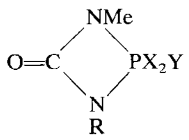
The ionization potentials of a series of *N*-methyl,*N'*-R-1,2,4-phosphadiazetidine-3-ones and related compounds have been determined. The nature of the highest occupied orbital of the molecules and the use of empirical rules to rationalize the variations in the ionization potentials are discussed. The changes in the fragmentation patterns are related to the different low ionization potential site(s) in each molecule. The occurrence of various rearrangement ions are discussed on a similar basis.

As an extension of our previous work,[1–4] and in connection with our present work on empirical rules relating ionization potentials,[5,6] we have studied some *N*-methyl, *N'*-(R)-1,2,4-phosphadiazetidine-3-ones (**1–10**) which can be regarded as derivatives of *N,N'*-dimethylurea (R = Me) or *N*-phenyl, *N'*-methylurea (R = C_6H_5). The ionization potentials of these compounds, the nature of R and of the substituents on the phosphorus atom are given in Table 1.



1–10

Table 1. Nature and ionization potentials (eV)[a] of compounds 1–10[b]

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
R	Me	Me	Me	Me	Me	Me	Me	C_6H_5	C_6H_5
X	F	F	F	Me	F	F	Cl	F	F
Y	F	Me	Et	F	C_6H_5	NEt_2	Cl	Me	Et
I(M)	9.60	9.00	8.90	8.70	8.80	8.85	9.20	8.15	8.00

[a] Values rounded off to 0.05 eV reproducibility ±0.10 eV.
[b] I(M) for **10** (R = Me), the substituents on phosphorus being F, Me and C_6H_5, was not measurable.

The nature of the highest occupied molecular orbital (HOMO) in these compounds can be deduced as follows. Our electron impact value for $I(PF_3)$ is 11.65 eV, which is in good agreement with other results determined by electron impact and photoionization methods.[7] This, together with the reported value of 13.40 eV[8] for $I(POF_3)$, seems to rule out a major involvement of the orbitals associated with the PF_3 group in the HOMO of **1**. Electron impact values of 10.60 and 10.75 eV[9] for $I(PCl_3)$ seem to rule out a major involvement of the orbitals associated with the PCl_3 grouping in the HOMO of **7**. The difference between I(**2**) and I (**3**) is typical of the effect observed elsewhere for methylation remote from the major orbital involved in the HOMO,[5] thus ruling out a major contribution to the HOMO in **4** by the $PFMe_2$ grouping. Since in *N,N'*-dimethylurea itself the HOMO seems to involve a major contribution from the nitrogen lone pair[5] it seems likely that a similar situation occurs in the compounds **1–4** and **7**. This is probably also true for **5** since $I(C_6H_6)$ in our case is 9.70 eV[6], and the effect of a PF_2 group next to this, if any, would be to increase the ionization potential .[7a] In the case of **6** it seems likely that the lone pair of the diethyl nitrogen substituent is involved in the HOMO since $I(Et_2NH)$, 8.44 eV[10], is lower than that of CH_3NH_2 (I(M) = 9.45 eV,[5] 9.41 eV[10]). In the cases of compounds **8** and **9**, the lower ionization potentials, which are similar to that for *N*-phenyl,*N'*-methylurea (I(M) = 8.50 eV[6]) suggests that the aromatic nucleus's orbitals are a major contributor to the HOMO.

It is interesting to note that the group additivity rules tentatively suggested by Cardnell *et al.*[5] for the calculation of ionization potentials when the lone pair of a nitrogen is involved in the HOMO do not work so well for compounds **1–9**. Thus, in (1) and (2) C and C' would be expected to be zero, whereas they are 0.20 and 0.15 eV, respectively. Slightly larger discrepancies are observed

$$I(N,N'\text{-dimethylurea}) - I(\mathbf{2}) = I(N\text{-Phenyl},N\text{-methylurea}) - I(\mathbf{8}) - C \quad (1)$$

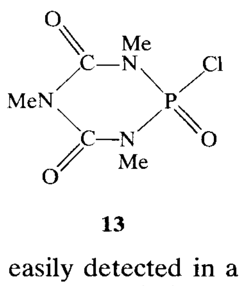
$$I(N,N'\text{-dimethylurea}) - I(\mathbf{3}) = I(N\text{-Phenyl},N'\text{-methylurea}) - I(\mathbf{9}) - C' \quad (2)$$

elsewhere.[6] The fact that a substituent has less effect on the ionization potential of a species in which the HOMO is extensively delocalized is not surprising.

The ionization potentials of sym. $(MeNPF_3)_2$ (**11**), 9.80 eV, and $((Me)_2N)_2PF_3$ (**12**), 8.80 eV, provide a better example of the application of these rules.[5] Thus, the difference between I(*N,N'*-dimethylurea), 9.40 eV, and I(**1**), using this approach, would be described as the difference between having two hydrogens, one on a nitrogen whose lone pair orbital is involved extensively in the HOMO, the other on a nitrogen β to the first nitrogen, and having a bidentate PF_3 grouping attached to both of these nitrogens instead. The change in the ionization potential on successive methylation on the nitrogen(s) β to the nitrogen whose lone pair is involved in the HOMO is small. Additionally, it is independent to a first order of the nature of the group between those two nitrogens. Thus, to calculate $I(\mathbf{11})-I(\mathbf{12})$ the changes in ionization potentials corresponding to the following transformations must be added together: (1) replacement of the two methyls, one on each nitrogen of **12**, by two hydrogens and (2) replacement of the two hydrogens by the PF_3 group. This would be expected[5] to increase the ionization potential by 0.55 eV, $(\Delta I_2-\Delta I_1)$,[5] and 0.15 eV, (ΔI_β), for step (1) and by taking the difference between I(*N,N'*-dimethylurea) and I(**1**) for step (2) a total of 1.10 ± 0.30 eV is obtained. This is in good agreement with the observed difference.

Since I(*N,N'*-dimethylurea) − I(**11**) is twice the difference between I(*N,N'*-dimethylurea) and I(**1**) this suggests that the nature of the intervening α groups does not alter the effect of changing the substituents on the nitrogen β to the nitrogen whose lone pair orbital is involved in the HOMO.

Before discussing the fragmentation patterns (in which all ions discussed have had their formulae confirmed by accurate mass measurement) of these molecules, in view of the known thermal instability of these compounds,[11,12] it is necessary to rule out thermolysis and subsequent ionization as a major source of some of the fragment ions observed. Two main pyrolytic pathways must be considered. At 180 °C under high vacuum, giving conditions similar to those existing in the heated inlet of the mass spectrometer when held at this temperature, compound **7** decomposes to give **13**[11] and we have obtained evidence that others of these compounds can behave similarly. The mass spectrum of **13** shows an intense molecular ion and hence it would be easily detected in a spectrum of **7**. Little or no trace of **13** or similar compounds were found in the spectra used in the following discussion.



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The other main pathway is decomposition in inert solvents, or the neat liquid. (It is necessary to consider this decomposition as the time between sample preparation and analysis was sometimes unavoidably long and some samples had completely decomposed.) In the case of **7** this gives[11] dimethylcarbodiimide and phosphorus oxychloride. Unfortunately two of the main ions in the spectra of these compounds (1–7), at *m/e* 70 (*a*, $C_3H_6N_2$) and at *m/e* $(M-C_3H_6N_2)$; the ion *b*, correspond to the molecular ions of the thermolysis products. In the case of compounds **8** and **9** the ions of *m/e* 132 and (M − 132), *a'* and *b'*, respectively, could also be produced in the same way. The other major primary fragment ions in these compounds are $[M-R'NCO+H]^+$, $[M-R'NCO]^{+\cdot}$ and $[M-R'HNCO]^+$ ($R'=Me$ or C_6H_5, **8** and **9** only). The second of these ions corresponds to the molecular ion of a possible intermediate[12] in the solution pyrolysis of **7**. Furthermore, the third of these ions could be produced from the second and indeed on lowering the electron voltage the intensity ratio $[[M-RNCO^{+\cdot}]]/[[M-RHNCO]^+]$ increases.

In our previous communication[13] we presented intensity and metastable evidence which ruled out prior thermolysis as a major source of the ions *a* and *b* in the case of compounds **2**–**5** and **7**. In the case of compounds **8** and **9** similar evidence for the ions *a'* and *b'* allows the same conclusion to be drawn. Since the possible pyrolysis intermediate for the $[M-RNCO]^{+\cdot}$ ion is an intermediate in the thermal production of the neutral molecule, corresponding in principal to *a* or *a'*, it seems that pyrolytic production of the $[M-RNCO]^{+\cdot}$ ion can be ruled out. In the case of compounds **1** and **10** all the evidence suggested that the spectra obtained were mainly of pyrolysis products and thus these compounds will not be discussed further.

In apparent contradiction to the conclusion that the spectra obtained in the case of compounds **2**–**9** were essentially not those of pyrolysis products, it was found that the appearance potential $A[a]^{+\cdot}$ of *a* in the case of compounds **2** and **7** was the same as I(*m/e* 70) found in the pyrolysis products of **7**. The most likely explanation is that this fragmentation reaction is a low energy process and this, coupled with the presence of a small amount of pyrolysis products, has reduced the observed appearance potential below the correct one.[15,14]

In terms of the simple older charge localization and fragmentation theories[1] for these compounds cleavage of the carbonyl–carbon–nitrogen bond, the nitrogen–phosphorus bonds or loss of one of the substituents on the phosphorus are equally likely, all being formally α-cleavages. However, the last of these only occurs to any appreciable extent in the case of **7**. Insofar as one can judge by ion intensities the most important primary fragmentation, producing the ions *a* and *b*, is one which involves cleavage of the phosphorus–nitrogen bond. This indeed, from the following evidence, would seem to be the weaker of the two ring bonds. Thus, for phosphoramide, *N,N'*-tetramethyl and hexamethylphosphoramide $A[M-NR_2]^+-I(M)$, $E_s[M-NR_2]^+$, is about 1.8 eV when $R=H$, except for the last compound where $R=Me$.[2] Values for $E_s[M-NR_2]^+$ in the ureas and thioureas are 3.0 eV or greater.[2] Thus, it would be expected that the P–N bond is weaker than the C–N bond in the molecular ions of compounds **2**–**9**.

The % Σ_{28} values of the molecular and common fragment ions for compounds **2–9** are given in Table 2. In the case of the *N,N'*-dimethyl compounds (**2–7**) the intensity ratio *a*/*b* and the overall importance of these ions decreases rather irregularly as the fluorines on the phosphorus are replaced. The importance of the $[M-RHNCO]^{+}$ ions also decreases in an irregular way. This can be correlated with the fact that the replacement of the fluorines on the phosphorus atom by less electronegative groups lowers the ionization potential of the phosphorus grouping.[7] Assuming that the activation energy (E_a) for any corresponding hypothetical reaction in the neutral compound (i.e. giving B and not $[B]^{+}$) stays constant, then from (3) the value of $A[B]^{+}$

$$A[B]^{+} = E_a + I(B) \tag{3}$$

decreases as the ionization potential of B decreases. Similar remarks apply to subsequent fragmentations. Thus, the presence of a second site with a low ionization potential may result in secondary reactions being enhanced. This effect is exemplified by the following fragmentations in these molecules. In the case of compounds **2**, **4**, **5** and **6** the $[M-CH_4NCO]^{+}$ ions all lose† (m^*) $(NCH)_2$ to give the ion $[PX_2Y]^{+\cdot}$. In compound **3** this ion $[M-CH_4NCO]^{+}$ decomposes by the loss of ethylene. The % Σ_{28} values for these ions are 0.1, 7.4, 2.8 and 2.0, respectively. The ionization potentials of the PX_2Y ion might be expected to decrease in the order $PMeF_2$, PMe_2F, $PC_6H_5F_2$ and PF_2NEt_2.[7] The drop in the intensity of the $[PX_2Y]^{+\cdot}$ ions in the last two cases, which is not in keeping with the above ionization potential order, probably reflects further fragmentations of this ion or alternative fragmentations of its precursor ions. Thus, in the case of **5** the high % Σ_{28} values for $Y(=C_6H_5)$ and for the subsequent fragment ions (*m*/*e* 52 and 51) of 12.0 and 8.1 would explain the drop. This alternative fragmentation is due to the low ionization potential of the phenyl radical. In the case of **6** the formation of the ions $[C_4H_{10}N]^{+}$ and $[C_4H_9N]^{+\cdot}$, % Σ_{28} 2.9 and 5.9 respectively, would explain the intensity drop. One other example of this ionization potential effect is the intensity ratio $[M-MeNCO]^{+\cdot}/[M-C_6H_5NCO]^{+\cdot}$ which for **9** rises from 2 at a nominal 70 eV to 20 at a nominal 13 eV. The $(M-MeNCO)$ neutral species would be expected to have a lower ionization potential than the $(M-C_6H_5NCO)$ neutral species. The increase in the ratio on lowering the electron energy is presumably due to easier decomposition of the $[M-MeNCO]^{+\cdot}$ species at higher energies.

Table 2. % Σ_{28} values for the molecular ion and common fragment ions[a] in the spectra of compounds 2–9

Ion/compound	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
$[M]^{+\cdot}$	1.0	2.1	4.1	0.6	1.0	0.5	0.6	0.6
a or *a'*	32.2	29.0	17.0	11.2	8.6	10.9	15.0	11.6
b or *b'*	1.1	0.2	1.0	22.0	0.5	4.7	4.7	0.5
$[M-R'NCO]^{+\cdot}$	1.1	3.5	2.6	1.5	1.2	5.5	1.3(1.5)	2.0(1.0)
$[M-R'HNCO]^{+\cdot}$	34.8	9.7	16.4	5.6	—	6.5	— (2.7)	— (1.5)
$[R'NCO]^{+\cdot}$	—	3.1	6.0	1.0	2.7	3.7	1.7(10.2)	0.9(7.0)
$[PX_2Y]^{+\cdot}$	—	—	7.4	2.8	2.0	—	—	2.6
$[PX_2]^{+\cdot}$	—	—	3.7[b]	—	—	4.0	3.1	—
$[R'NPX_2Y]^{+\cdot}$	3.0	13.7	—	—	—	4.3	—	—

[a] In compounds **2–7** R' = Me; in compounds **8** and **9** the values in parentheses are for $R' = C_6H_5$ and the others for R' = Me.
[b] In this case the ion is $PFCH_3$.
— signifies less than 0.5% Σ_{28} (% Σ_{28} is the ion intensity expressed as a % of the total ion intensity from *m*/*e* 28).

These observations could equally well be explained by the hypothesis[17] of Howe and Williams which assumes that the introduction of lower ionization potential sites reduces the relative number of molecular (or fragment) ions with the charge located in the position which induced the original fragmentation. This would reduce the amount of this fragmentation.

As a result of the accidental determination of the mass spectrum of the decomposition products of **10** the behaviour of fluorophenylmethylphosphorus oxide was investigated. The molecular ion decomposes to give a $[C_7H_7]^{+}$ ion. Investigation of dimethylphenylphosphorusthio-oxide showed that the 'same' ion was formed from the $[M-HS]^{+}$ ion (m^*). This ion was also present in the spectrum of phenyldimethylphosphine and in the spectra of diphenyldifluoromethylphosphane and trifluorophenylmethylphosphane, but only in the first compound was there a metastable connecting the molecular ion to this ion. The absence of a metastable in the last two compounds could be due to the other rearrangement ions which were observed. In the case of diphenyl compounds an $[M-C_6H_5F]^{+\cdot}$ ion, $[C_6H_5PFMe]^{+\cdot}$, is formed from the molecular ion (m^*), whereas in the monophenyl compounds a $[C_6H_5F]^{+\cdot}$ ion is formed from the molecular ion (m^*). The difference in charge location in these two cases can be rationalized as follows. The neutral species MeF_2P, which is ejected in the formation of the C_6H_5F ion from the monophenyl compound is likely to have a higher ionization potential than that of fluorobenzene (9.75 eV[6]), since $I(PF_3)$ is 11.65 eV. In the case of the diphenyl compound the neutral species corresponding to the $[M-C_6H_5F]^{+\cdot}$ ion, i.e. C_6H_5PFMe, is likely to have a lower ionization potential than fluorobenzene. This conclusion is reached from the observation that fluorine has little effect on the ionization potential of benzene (9.70 eV[6]) and with the fluorine further removed will have little effect at all. In the case of compound **2**, with a PF_2Me grouping I(M) is lower than I(*N,N'*-dimethylurea), which would suggest that the PFMe grouping will lower the ionization potential of the aromatic nucleus in the compound C_6H_5PFMe compared with benzene. Thus, it is not surprising that the $[C_6H_5F]^{+\cdot}$ ion is missing in the case of the diphenyl compound. This argument assumes that the mode of formation of the two ions in each individual case would be the same with the exception of the charge location. This argument is essentially an extension of Stevenson's rule.

EXPERIMENTAL

All samples were introduced via the heated inlet system of an AEI. MS-902 mass spectrometer held at c. 100 °C and the data were recorded at 70 eV unless

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† m^* denotes that a metastable was observed in the 2nd field free region.

otherwise specified. Ionization and appearance potentials were determined in the usual manner[17] except that the low absolute intensities of the molecular ions, caused partially by the necessity of keeping the sample inlet system temperature low enough to avoid pyrolysis, made it necessary to normalize the molecular ion currents at 5000 and not 10 000 units.[17]

The preparation of these compounds has been reported elsewhere.[18]

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