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PHOTOELECTRON SPECTRA OF MOLECULES—IV

IONIZATION POTENTIALS AND HEATS OF FORMATION OF SOME HYDRAZINES AND AMINES*

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Abstract—The ionization potentials for several hydrazines and amines have been measured from their photoelectron spectra. The photoelectron spectrometer employed in this study was of the low resolution retarding potential type and has been recently described.[1] The first ionization potentials (I_1) and heats of formation for these molecules have been calculated by the recently developed[2] MINDO/2 SCF MO method. Estimates of the vertical ionization potentials have been made by comparing the heats of formation of the molecules and of the ions derived from them.[3]

EXPERIMENTAL geometries were used in the MINDO/2 calculations whenever data were available[4] (e.g. 1,1-dimethylhydrazine, 1,2-dimethylhydrazine); otherwise the geometries were assumed to be similar to those of analogous molecules (e.g. toluene, aniline). In all cases the conformation was assumed to be the one expected on theoretical grounds to be the most stable.** In the calculations for ions, the geometry was perforce assumed to be the same as for the parent molecule, the calculated ionization potentials being consequently vertical, not adiabatic.

A typical spectrum is shown in Fig 1. The ionization potentials derived from breaks in the photoelectron spectra, and the MINDO/2 values for I_1, are listed in Table 1. The last two columns of Table 1 show the calculated heats of formation of the molecules and the derived ions.

Very few measurements of ionization potentials have been reported for these compounds. Franklin *et al.*[5] have described electron impact studies of I–VI (Table 1) leading to the following values for I_1 (eV):

I, 9·00; II, 8·63; III, 8·12; IV, 7·75; V, 7·93; VI, 7·76

While these values show the same downward trend as ours with increasing Me substitution, they seem to be systematically too low; for the electron impact appear-

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** For the hydrazines the dihedral angle between the two lone pairs was chosen to be 60°.

TABLE 1. IONIZATION POTENTIALS AND HEATS OF FORMATION FOR SOME HYDRAZINES AND AMINES

Molecule	First ionization potential[a]			Observed higher ionization potentials[a, e]	ΔH_f° (298°K)[b]	
	Obs.	Calc.[c]	Calc.[d]		Molecule	Ion
I. Hydrazine	8·93	9·72	9·48	(9·32), 14·80, 16·44, (19·65)	17·0	235·6
II. Methylhydrazine	8·67	9·51	9·03	(9·04), 9·88, 12·81, (13·16), 15·50, (19·61)	20·8	229·1
III. 1,1-Dimethylhydrazine	8·28	9·48	8·82	(8·60), 9·77, 12·35, (12·72), 16·45, (19·13)	30·8	234·2
IV. 1,2-Dimethylhydrazine	8·22	9·40	8·78	(8·70), (11·57), 12·04, (12·45), (13·23), 15·53, (16·97), (19·03)	24·8	227·4
V. Trimethylhydrazine		9·30	8·64		39·4	238·7
VI. Tetramethylhydrazine	7·93	9·05	8·50	(8·24), 11·91, (18·69)	59·6	255·7
VII. Phenylhydrazine	7·74	8·72	8·22	9·12, 10·52, 11·52, (11·84), 13·71, 15·38, 16·58	54·6	244·2
VIII. 1-Methyl-1-phenylhydrazine	7·43	8·71	8·15	8·97, 9·79, 11·22, (11·53), (13·20), 13·68, 16·59, (18·58)	68·9	256·8
IX. Benzylhydrazine	8·64	9·10	8·59	(8·91), 11·31, 12·92, 13·59, 16·49, (18·61)	61·3	259·4
X. Aziridine	9·52	9·74	9·23	(9·78), 11·51, (11·79), 15·56, 16·97, 17·29, (19·51)	27·7	240·4
XI. 2,2-Dimethylaziridine	8·94	9·42	8·77	(9·24), 10·71, (10·98), 12·89, 16·59, (18·62)	13·9	216·1
XII. Benzylamine	8·73	9·19	8·77	11.22, (11·55), 12·82, 13·66, (14·87), 16·57	23·1	225·4
VIII. Dibenzylamine	8·22	8·51	7·93	8·73, 11·01, (11·43), 12·84, 13·62, 14·79, 16·53, (18·32)	93·7	276·6
IV. Dibenzylmethylamine	7·85	8·37	7·66	8·74, 10·89, (11·24), (12·40), (16·53), (18·57)	124·2	300·8

[a] All values are in eV.

[b] All values are in kcal/mole.

[c] Values estimated using Koopmans' theorem.

[d] ΔH_f° (ion)-ΔH_f° (molecule) (Vertical I_1).

[e] Values in parentheses are uncertain.

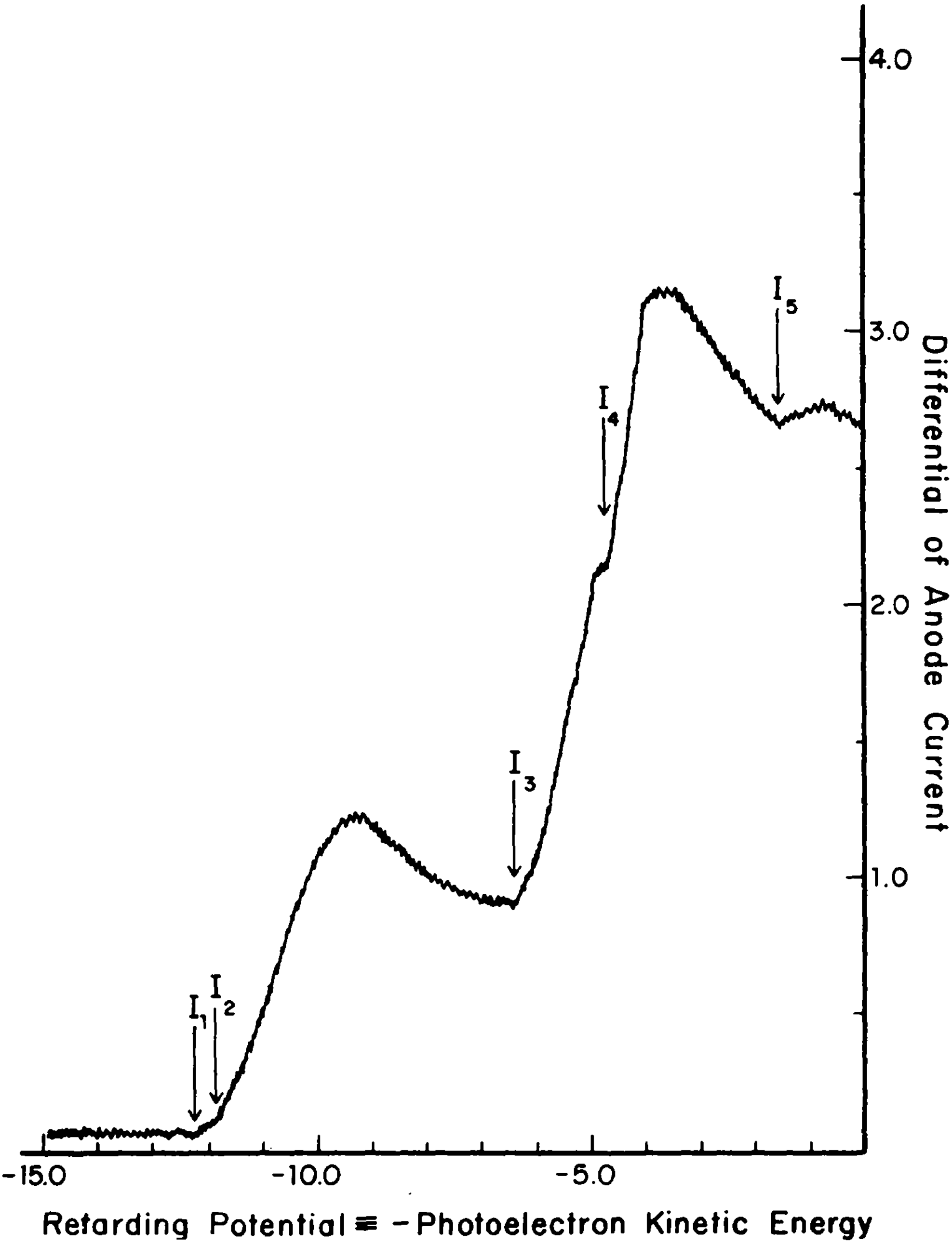

FIG 1. Photoelectron Spectrum of Hydrazine (p = 0·032 mm) excited by the 21·22 eV resonance line of helium.

ance potentials, corresponding to vertical ionization, should be greater than the adiabatic ionization potentials derived from breaks in photoelectron spectra.

The electron impact values for IV, V and VI are moreover clearly suspect, V and VI being greater than that for IV; all analogy, and our MINDO/2 calculations, agree in predicting that further methylation of IV, to V or VI, must lead to a decrease in I_1.

Vilesov and Terenin[6] have reported photoionization values of I_1 for I (9·56 eV), VII (7·64 eV), and XII (8·64 eV). Those for VII and XII are in reasonable agreement with ours, but that for I is greater by 0·63 eV. The latter must almost certainly be incorrect, being 0·56 eV greater than the electron impact value (9·00 eV[5]).

Turner *et al.*[7] have reported a value of 9·8 eV for I_1 of X from the high resolution photoelectron spectrum; since this was a vertical value, derived from the maximum in the I_1 band, the agreement with our adiabatic value (9·52 eV) is good. We saw no indications of breaks in our low resolution spectrum at 10·6 or 14·9 eV; Turner *et al.*[7] observed weak peaks of these potentials but attributed them to impurities.

Table 1 shows values for I_1 found by difference between the MINDO/2 heats of formation for molecules and ions, and from the orbital energies using Koopmans' theorem. The former agree much better with experiment; the agreement is indeed remarkably good, given that the calculated values, being vertical, should be 0–0·3 eV greater than the measured adiabatic ones. The discrepancies in the case of IX–XIV, where the calculated values are less than those observed, may well be due to the use of arbitrary geometries or to ring strain, for which MINDO/2 does not account adequately. Note, however, that the calculations correctly predict that I_1 for the aziridines X and XI should be greater than that for an open chain secondary amine (e.g. XIII); in the case of hydrocarbons, ring strain leads to a decrease in I_1, also correctly[2] predicted by MINDO/2.

The MINDO/2 calculations predict the "lone pair" electrons in all of these molecules to be moderately delocalized; this would account for the diffuseness of the I_1 breaks in many of the spectra, I_1 corresponding to removal of a "lone pair" electron. If the lone pair electrons were localized, ionization would lead to little or no change in geometry and the breaks in the photoelectron spectrum would then be very sharp. Vilesov and Terenin[6] have likewise reported low quantum yields for photoionization of aromatic amines at wavelengths near the ionization threshold.

Heats of formation have been reported for only four of the compounds studied here; for these the experimental values (I, 22·75[8]; II, 23·35[9]; IV, 22·80[10]; X, 30·1[11] kcal/mole) are in reasonable agreement with the MINDO/2 ones (Table 1).

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