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GROUND STATES OF σ-BONDED MOLECULES—VIII*

MINDO CALCULATIONS FOR SPECIES INVOLVED IN NITRATION BY ACETYL NITRATE†

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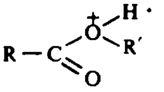
Abstract—It is shown that the MINDO semiempirical SCF MO method gives good values for heats of formation of inorganic species and ions as well as neutral molecules. Calculations are reported for the various species that could be involved in nitrations by nitric acid in acetic anhydride; it is concluded that the active agent is protonated acetyl nitrate, and that the acetoxylation and addition reactions are due to acetyl nitrate protonated at the ether-type oxygen.

NITRIC acid in acetic anhydride was first used as a nitrating agent by Orton,[1] and the properties of this reagent were shortly afterwards shown[2] to be the same as that of an acetic acid solution of acetyl nitrate (I), prepared from acetic anhydride and nitrogen pentoxide. However although this reagent has been extensively used in the preparation of aromatic nitro compounds and nitric esters,[3] and although it has often been used to compare the reactivities of different aromatic systems to electrophilic substitution,[4] the nature of the actual nitrating agent and its mode of action are still in doubt.

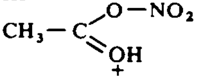
Two additional facts that must be accommodated by any suggested mechanism are the production of 2-nitro-1-alkyl acetates by *cis* addition of I to olefines,[5] and the fact that I under certain conditions behaves as an acetoxylating, rather than nitrating, species. Thus the major product from o-xylene is 3,4-dimethylphenyl acetate,[6] smaller amounts of nitroxylenes also being formed. All these reactions seem moreover to be acid catalyzed.

It is usually assumed that protonation of carboxylic acid derivatives takes place preferentially at the carbonyl oxygen, the resulting cation (II) being mesomeric;

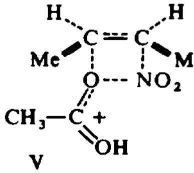
II



III



IV



V

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* For the previous paper in this series (in future referred to as Part VII) see M. J. S. Dewar, M. Shanshal and S. D. Worley, *J. Am. Chem. Soc.* **91**, 3590 (1969).

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protonation of the ester oxygen would give a nonmesomeric cation (III). On this basis one might expect the active agent in acid catalyzed reactions of I to be the ion IV; however it is difficult to see how this could act as an acetoxylating agent, while the obvious one-step addition of IV to an olefine to give the observed *cis* adduct would involve a transition state (e.g. V) which would be antiaromatic,[7] being isoconjugate with cyclobutadiene.

Several investigations have on the other hand suggested that the active species in solutions of I in acetic acid is the nitronium ion,[8] NO_2^+, or nitrogen pentoxide,[9] N_2O_5, formed by the following reversible processes:

$$AcONO_2H^+ \rightleftharpoons AcOH + NO_2^+ \tag{1}$$

$$2AcONO_2 \rightleftharpoons Ac_2O + N_2O_5 \tag{2}$$

$$N_2O_5 \rightleftharpoons NO_2^+ + NO_3^- \tag{3}$$

Detailed study has, however, failed[10] to indicate the presence of any nitronium ion in any mixtures of nitric acid, acetic acid, and excess acetic anhydride, although it has been shown[11] that acetyl nitrate is formed under these conditions by the process:

$$Ac_2O + HNO_3 \rightleftharpoons AcONO_2 + AcOH \tag{4}$$

It has also been shown[12] that the conversion of steroid alcohols to their nitric esters almost certainly involves an intermediate species derived from the protonation of I.

Recently a semiempirical SCF MO treatment (MINDO method*[13]) has been developed here which seems to provide good estimates of the heats of formation of compounds of all types composed of carbon, hydrogen, nitrogen, and oxygen, other than those containing triple bonds. It is necessary to assume geometries based on standard bond lengths and bond angles, since the procedure in its present form does not predict bond lengths correctly; this, however, does not affect its use for calculating equilibria since these depend on differences in energy between stable species. We have accordingly carried out calculations of this kind for the various compounds that might be involved in the reactions of acetyl nitrate in the hope of obtaining further information concerning their mechanisms.

THEORETICAL PROCEDURE

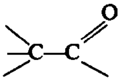
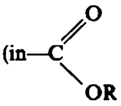
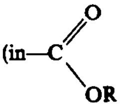
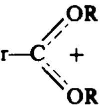
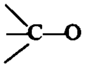
The calculations were carried out by the MINDO method, using the parameters suggested previously.*[13] In calculating molecular geometries, it was assumed that all quadruply linked atoms have tetrahedral geometry, and all triply linked ones planar geometries with 120° bond angles. The assumed standard bond lengths are listed in Table 1.

RESULTS

The MINDO method has so far been applied only to neutral organic species; our first objective was to see whether or not it could usefully be applied in connections such as the present one, where ions and inorganic species are involved. Table 2 compares calculated and observed heats of formation for a number of relevant species, where such data are available; the agreement is clearly very satisfactory,

* See footnote * on page 5777.

TABLE 1. STANDARD BOND LENGTHS

Bond	Bond type	Bond length (Å)
C—H	sp^3-H	1·093
	sp^2-H	1·083
C—C	sp^3-sp^3	1·534
	sp^2-sp^3	1·520
		1·506
C—O	C=O (in 	1·245
	C—O (in  or 	1·315
		1·426
	C=O (in $C{=}\overset{+}{O}H$)	1·280
N—O	N—O	1·460
	N=O	1·200
	N=O (in —NO_2)	1·273
O—H	O—H	0·970

particularly since the experimental values for the heats of formation of the ions in the gas phase are still somewhat uncertain.

Next we needed to know if our procedure could be relied on to predict protonation reactions; to do this, it would need to predict the heats of formation of the conjugate acids formed by protonation of bases. The calculations refer of course to the gas phase, where such data are scanty; Table 3 compares calculated and observed values where these are available, together with corresponding proton affinities (i.e. the energy liberated when gaseous base combines with a free proton). The agreement is again very good.

Finally we calculated heats of formation and proton affinities for the remaining species of interest in the present connection; the results are shown in Table 4.

DISCUSSION

Using the heat of formation calculated for acetyl nitrate (Table 4), we can calculate the heat of reaction for the process indicated in Eq. (4); we find:

$$Ac_2O + HNO_3 \rightarrow AcOH + AcONO_2; \quad \Delta H = -6{\cdot}0 \text{ kcal/mole} \qquad (5)$$

TABLE 2. HEATS OF FORMATION (ΔH_f) IN THE GAS PHASE AT 25°

Compound	ΔH_f (kcal/mole)			Ref.
	calc.	obs.	error	
Acetic anhydride	−143·10	−138·10	4·9	*a*
Nitric acid	−32·92	−32·20	0·7	*b*
Acetic acid	−102·59	−103·80	1·2	*c*
CH_3COO^-	−110·00	−116·84	—	*b, d*
NO_3^-	−70·48	−89 ± 5	18 ± 5	*e*
NO_2^+	231·10	244·5 ± 5	13 ± 5	*e*
N_2O_5	−0·34	3·35	3·7	*f*
N_2O_4	2·70	2·54	0·2	*f*
	3·71			*g*

[a] H. S. Green, *Quart. Rev.* **15**, 125 (1961).

[b] Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards, Washington, D.C. (1952).

[c] N. C. Baird, M. J. S. Dewar and R. Sustmann, *J. Chem. Phys.* **50**, 1275 (1969), calculation, and Ref. of Note *a*.

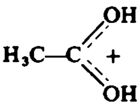
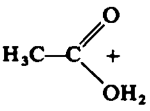
[d] In standard state.

[e] H. F. Cordes and N. R. Fetter, *J. Phys. Chem.* **62**, 1340 (1958).

[f] I. C. Hisatsune, *Ibid.* **65**, 2249 (1961).

[g] For the coplanar molecule.

TABLE 3. PROTON AFFINITIES (PA) OF OXYGEN COMPOUNDS AND HEATS OF FORMATION (ΔH_f) OF THEIR CONJUGATE ACIDS

Base	Ion	ΔH_f (kcal/mole)		PA (kcal/mole)[a]	
		calc.	obs.	calc.	obs.
CH_2O	$H_2C{=}\overset{+}{O}H$	174·25	175^b; 176 ± 3^c	163	163^b; 161 ± 3^c
CH_3CHO	$CH_3CH{=}\overset{+}{O}H$	148·80	143^b; 145 ± 3^c	180	182^b; 180 ± 3^c
CH_3COOH	(a) 	78·28		183	
			75 ± 3^c		184^b; 184 ± 3^c; 180^d
	(b) 	72·90		188	
H_2O	H_3O^+	146·92	157 ± 3^c	161	167^b; 151 ± 3^c; 160^e
CH_3OH	$CH_3\overset{+}{O}H_2$	127·20	$\sim 150^b$; 136^f	190	$\sim 167^b$; 180^e; 180^f

[a] Calculated using $\Delta H_f(H^+) = 365$ kcal/mole.

[b] M. S. B. Munson and J. L. Franklin, *J. Phys. Chem.* **68**, 3191 (1964).

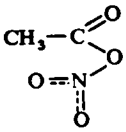
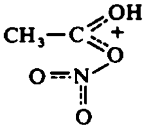
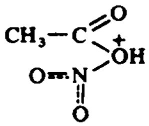
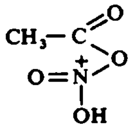
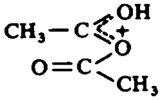
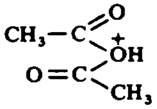
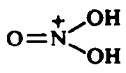
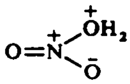
[c] A. G. Harrison, A. Ivko and D. Van Raalte, *Canad. J. Chem.* **44**, 1625 (1966).

[d] E. W. Godbole and P. Kebarle, *Trans. Faraday Soc.* **58**, 1897 (1962).

[e] R. P. Bell, *The Proton in Chemistry*, Chap. IV. Cornell University Press, Ithaca, N.Y. (1959).

[f] V. L. Tal'roze, *Pure Appl. Chem.* **5**, 455 (1962).

TABLE 4. CALCULATED HEATS OF FORMATION (ΔH_f) AND PROTON AFFINITIES (PA) FOR INDICATED GEOMETRIES

Compound	ΔH_f (kcal/mole)	PA (kcal/mole)[a]
	−72·49	—
	119·59	173·2
	117·39	175·4
	140·27	152·5
	24·56	197·3
	23·30	198·5
	185·37	147·4
	165·56	167·2
CH_3CO^+	231·15	—

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[a] For formation of indicated ion from parent base.

Since the changes in entropy and heat of solvation are likely to be small, we would therefore expect the equilibrium for a solution of nitric acid in excess acetic anhydride to lie well over to the right, in agreement with experiment.[11]

No experimental value has been reported for the heat of this reaction, but the equilibrium constant (k) has been measured[11] at several different temperatures. A plot of log k vs $1/T$ gives an excellent straight line from which ΔH can be estimated; the value found in this way ($-5{\cdot}70$ kcal/mole) agrees almost exactly with our prediction.

Next let us consider the equilibria of Eqs (1) and (2). Using the experimental heats of formation from Table II, and the calculated heats of formation of acetyl nitrate and its conjugate acid from Table 4, we find:

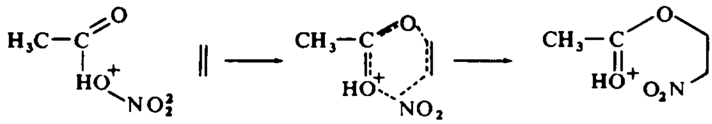
$$\mathrm{AcONO_2{\cdot}H^+} \rightarrow \mathrm{AcOH} + \mathrm{NO_2^+}; \quad \Delta H = +23{\cdot}3\ \text{kcal/mole} \tag{6}$$

$$\mathrm{2AcONO_2} \rightarrow \mathrm{Ac_2O} + \mathrm{N_2O_5}; \quad \Delta H = +10{\cdot}1\ \text{kcal/mole} \tag{7}$$

Both processes are predicted to be strongly endothermic in the gas phase; the heats of reaction are probably reasonably reliable, given our success in predicting the heat of reaction for Eq. (5) and the proton affinities in Table 3. In the case of Eq. (7), a simple redistribution reaction, the entropies and energies of solvation should be similar for both reactants and products; the free energy of reaction is therefore likely to be also of the order of $+10$ kcal/mole. In the case of Eq. (6), the solvation energy of the reactants is likely to be greater than that of the products since $\mathrm{AcONO_2{\cdot}H^+}$ should form especially strong H-bonds to the solvent; the free energy of reaction in solution is therefore likely to be even greater than the gas phase value for ΔH.

It is of course well known that nitration by acetyl nitrate can be an extremely facile reaction, the rates in the case of reactive substrates being too fast to measure by conventional means even at low temperatures. This seems to rule out $\mathrm{NO_2^+}$ as an intermediate, given that its formation is predicted to be endothermic by 23·6 kcal/mole. It also seems to rule out $\mathrm{N_2O_5}$ as the active species; for while its formation is predicted to require less energy than that of $\mathrm{NO_2^+}$, its subsequent reaction with the aromatic substrate would certainly require considerable activation, being a bimolecular reaction between neutral species leading to ionic products. If, as these arguments suggest, the active nitration species is neiter $\mathrm{NO_2^+}$ nor $\mathrm{N_2O_5}$, it seems difficult to suggest any alternative other than a protonated form of acetyl nitrate.

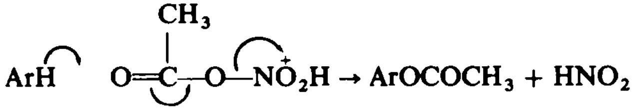
Now the calculations in Table 3 and 4 lead to a rather expected conclusion, that the preferred point of attachment of a proton to an acetic derivative is *not* the carbonyl oxygen. Acetic acid, acetic anhydride, and acetyl nitrate are all predicted to protonate most easily at the ether-type oxygen, although the difference from carbonyl is small. This suggests that the species responsible for addition to olefines, and acetoxylation of xylene, is acetyl nitrate protonated at the central oxygen, the reactions being conventional electrocyclic additions taking place with transition states containing 6-membered aromatic rings; i.e.



(8)

In the case of xylene, the aromatic ring is of course regenerated by elimination of nitrous acid. The reaction is thus formally analogous to the Diels–Alder reaction and the role of the proton analogous to that of Lewis acids in the addition of dienes to maleic anhydride and other dienophiles.[14] Reactions of this type take place more easily, the greater the difference in electronic character between diene and dienophile. Thus electrophilic dienophiles react most easily with nucleophilic dienes, and nucleophilic dienophiles with electrophilic dienes; an acid catalyst operates by making the electrophilic member of the pair still more electrophilic, with a consequent increase in polarization of the mobile electrons in the cyclic transition state.[7b]

The normal nitration reactions of I could also be due to the same species; they could, however, equally well be due to attack by the almost equally stable conjugate acid formed by protonation of the carbonyl oxygen of I. In either case, the reaction is essentially an S_N2 displacement of acetic acid from $(I—H)^+$, the aromatic compound behaving as the nucleophilic reagent. Note incidentally the very high energy of the species formed by the protonation of I at the nitro oxygen; the corresponding conjugate acid is unlikely to play any role in the reactions of I, although its intervention would provide a very simple mechanism for acetoxylation, i.e.



$$\mathrm{ArH}\quad \mathrm{O{=}\overset{CH_3}{\overset{|}{C}}{-}O{-}\overset{+}{N}O_2H} \rightarrow \mathrm{ArOCOCH_3} + \mathrm{HNO_2} \qquad (9)$$

The prediction that carboxylic acid derivatives should protonate easily at the ether oxygen is not in fact as surprising as it might seem to be at first sight. Protonation of oxygen involves the formation of a dative bond to H^+, a process which can be dissected into an electron transfer follwed by formation of a covalent bond, viz.

$$>\!\mathrm{O}: + \mathrm{H}^+ \rightarrow\ >\!\overset{+}{\mathrm{O}}\cdot\ \ \cdot\mathrm{H} \rightarrow \overset{+}{\mathrm{O}}{—}\mathrm{H} \qquad (10)$$

The overall heat of this reaction should therefore be given by:

$$\Delta H_f = I_O - I_H - E_{OH} \qquad (11)$$

where I_O is the valence state ionization potential of the oxygen lone pair, I_H is the ionization potential of H (i.e. the electron affinity of H^+), and E_{HO} the bond energy. Now the valence state ionization potential of an sp^2 hybrid AO in carbonyl oxygen is much greater (by 2·26 eV, or 52·4 kcal/mole[15]) than that of an sp^3 hybrid AO in ether-type oxygen; carbonyl oxygen should therefore be inherently much less basic than ether oxygen, and the difference could well be enough to outweigh the resonance stabilization of ions such as II in comparison with III. It should be added that similar conclusions have been reached on the basis of MINDO calculations for the protonation of nitrous[1] and nitric acid derivatives, where the proton is again predicted to attach itself preferentially to the singly linked oxygen (cf. Table 3).

We also calculated the heat of formation of the acetylium ion, CH_3CO^+ (Table 4). Using this value, we can estimate the heat of dissociation of protonated acetic anhydride into acetic acid and acetylium;

$$(CH_3CO)_2\overset{+}{O}H \rightarrow CH_3COOH + CH_3C\overset{+}{O}; \quad \Delta H = +125\cdot5 \text{ kcal/mole} \qquad (12)$$

this process is clearly quite impossible, unless coupled with some appropriate reaction (e.g. protonation) of the acetic acid simultaneously formed. It is extremely unlikely that any acid catalysed reactions of acetic anhydride involve the formation of free acetylium ions as intermediates.

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[12] O. Mantsch and N. Bodor, *Ibid.* **14** (1969) in press.
[13] N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.* **50**, 1262 (1969); N. C. Baird, M. J. S. Dewar and R. Sustmann, *Ibid.* **50**, 1275 (1969).
[14] see Von J. Sauer, *Angew. Chem.* **79**, 76 (1967).
[15] J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.* **84**, 540 (1962).