Calculated and Observed Ionization Potentials of Nitroalkanes and of Nitrous and Nitric Acids and Esters.[1] Extension of the MINDO Method to Nitrogen–Oxygen Compounds

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Abstract: (a) A recently developed semiempirical SCF–MO procedure (MINDO method) has been extended to compounds containing nitrogen and oxygen. Calculations are reported for nitroalkanes and for nitrous and nitric acids and their esters. (b) The photoelectron spectra of these compounds have also been measured, using a grid-type retarding potential spectrometer; the observed first ionization potentials correlate well with the calculated energies of the highest occupied MO's. (c) The protonation of nitrous and nitric derivatives has been studied by the MINDO method; the calculations indicate that protonation should take place preferentially at the singly bound oxygen. This unexpected result is interpreted in terms of the effect of hybridization on the basicity of lone pair electrons.

Recent work in these laboratories has led to the development of a semiempirical SCF–MO procedure (MINDO method[3]) which gave excellent estimates of the heats of formation for a wide range of organic compounds containing nitrogen or oxygen. We have now extended these calculations to compounds containing both heteroatoms simultaneously, in particular to nitro compounds and to nitrous and nitric acids and esters.

An interesting feature of the MINDO method is the close correlation observed between the ionization potentials of molecules and the calculated orbital energies.[4] In the case of the compounds considered here, however, good experimental data were largely lacking;[5] we have therefore measured the photoelectron spectra of most of the compounds for which calculations are reported, using a grid-type retarding potential spectrometer described in an earlier paper.[4]

Theoretical Treatment

The MINDO method has been described in detail in two earlier papers;[3] the calculations reported here used the same parameters as before[3] for CH, CC, CN, CO, NH, NN, and OH interactions. In the MINDO method it is also necessary to use an assumed molecular geometry, calculated from standard values for bond angles and bond lengths. Here again the same values as before[3] were used when available. The additional parameters required in the case of compounds containing both nitrogen and oxygen refer solely to NO interactions; here the two-center repulsion integrals were calculated in terms of the corresponding one-center integrals using the expression given in part V,[3b] while the resonance integrals were given by eq 1 of part V[3b] with

$$\beta_{\mathrm{I}} = 0.26240 \qquad \beta_{\mathrm{II}} = 0.0545\ \text{Å}^2 \tag{1}$$

In SCF–MO methods, it is necessary to assume an initial charge density–bond order matrix to construct the F matrix for the first iteration. In the MINDO method,[3] it is normally assumed that the initial bond orders are zero, that the atoms are neutral, and that the total electronic charge at each atom is shared equally among the valence orbitals, *i.e.*

$$p_{\mu\nu} = 0 \qquad q_\mu^{\mathrm{A}} = C_{\mathrm{A}}/n_{\mathrm{A}} \tag{2}$$

where q_μ^{A} is the charge density in AO μ of atom A, and C_{A} and n_{A} are respectively the core charge and number of valence orbitals in atom A. However, when we used this procedure for compounds containing nitrogen directly linked to oxygen, the iterative SCF treatment frequently failed to converge; apparently the formal charges are so large, and the assumption that the atoms are neutral so poor an approximation, that the initial F matrix differs too greatly from the final SCF F matrix for convergence to the correct limit to be achieved. In order to allow for this, we assumed initial charge densities corresponding to a formal charge of +1 on any nitrogen atom directly linked to oxygen, and of −1 on any oxygen atom directly linked to nitrogen, *i.e.*

$$q^{\mathrm{N}} = (C_{\mathrm{N}} - 1)/n_{\mathrm{N}} = (5 - 1)/4 = 1 \tag{3}$$

$$q^{\mathrm{O}} = (C_{\mathrm{O}} + 1)/n_{\mathrm{O}} = (6 + 1)/4 = 1.75 \tag{4}$$

With these initial values, the SCF treatment converged in all cases, and it was established that the results were identical with those given by the standard procedure in cases where the latter converged.[6]

The additional geometrical parameters refer again to nitrogen and oxygen directly linked. It was assumed that the valence angles in doubly bound nitrogen are 120° and that the various bond lengths have the values

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[1] This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

[2] Mobil Fellow, 1968–1969.

[3] (a) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1269 (1969); (b) N. C. Baird, M. J. S. Dewar, and R. Sustman, *ibid.*, **50**, 1275 (1969).

[4] M. J. S. Dewar and S. D. Worley, *ibid.*, **50**, 654 (1969).

[5] Ionization potentials measured by electron impact are quite useless for this purpose since they are far too inaccurate; see ref 4.

[6] In cases where there are two or more oxygen atoms linked to a given nitrogen, the charge densities of eq 4 and 5 will of course lead to an initial bond order–charge density matrix in which the sum of the charge densities is greater than the total number of valence electrons. This does not matter, however, since the situation is corrected after the first iteration; the only requirement is that the initial charge density–bond order matrix should lead to an initial F matrix which is sufficiently close to the final SCF one for the iteration procedure to converge to it.

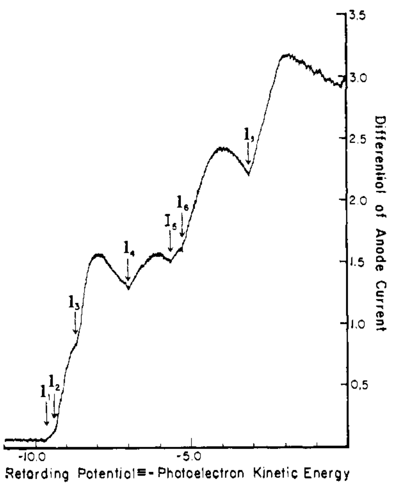
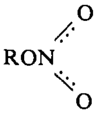
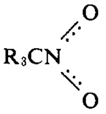


Figure 1. Photoelectron spectrum of methyl nitrate (p = 0.035 mm).

listed in Table I. These are within 0.02 Å of the ones recommended by Sutton in his compilation,[7] except for $-NO_2$; the value used here was chosen to fit the observed heat of formation of nitric acid.

Table I. Assumed Values for NO Bond Lengths

	Bond length, Å			
System[a]	N—O	N—O	N=O	C—N
RON=O	1.460		1.200	
 $\mathrm{RO}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{N}}}$	1.460	1.273		
 $\mathrm{R_3C}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{N}}}$		1.273		1.500

[a] R = H or alkyl.

Measurement of Photoelectron Spectra

Materials. The nitroalkanes were obtained from Aldrich Chemical Co. and methyl nitrate from K & K Laboratories. The alkyl nitrites were prepared by standard methods.[8] The physical properties of the compounds agreed with those reported previously; preparative glpc was used to purify all those with sufficient stability, and all the compounds were thoroughly degassed by cycles of freezing, evacuation, distillation, etc., before use.

The spectrometer was the grid-type retarding potential instrument described previously;[4] each compound was measured at least 12 times to ensure that the observed breaks in the spectrum were genuine. A typical spectrum (for methyl nitrate) is shown in Figure 1; the breaks corresponding to the first ionization potentials (I_1), and other major breaks in the spectra, were reproducible to ±0.01 eV, while even the weaker ones (*e.g.*, I_3 in Figure 1) were reproducible to better than ±0.05 eV.

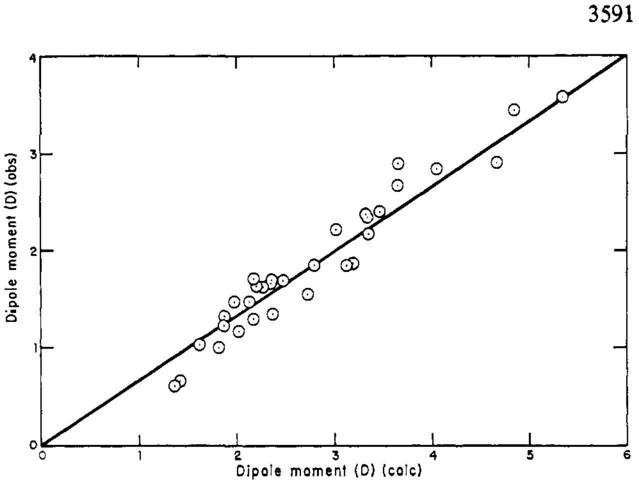


Figure 2. Plot of calculated *vs.* observed dipole moments for organic compounds of nitrogen or oxygen,[3] and for the compounds listed in Table II.

Results and Discussion

Heats of Formation and Dipole Moments. Table II compares the calculated and observed heats of formation of a number of compounds containing NO bonds. The agreement is about as good as that reported previously in other MINDO calculations.[3] In particular, the differences in heat of formation between isomeric pairs of nitroparaffins and alkyl nitrates is correctly reproduced, and also the order of stability in a series of isomeric nitroparaffins.

Table II. Heats of Formation and Dipole Moments of Nitrous and Nitric Acids and Esters and of Aliphatic Nitro Compounds

	Heat of formation, kcal/mol at 25°			Dipole moment, D	
Compd	Calcd	Obsd	Error	Calcd	Obsd
HONO	−18.76[a]	−18.84[b]	+0.1	3.13[a]	1.85[c]
MeONO	−17.87[a]	−14.93[d]	−2.9	3.03[a]	2.22[e]
EtONO	−22.32[a]	−24.20[d]	+1.9	3.33[a]	2.38[f]
n-PrONO	−27.00[a]	−31.26[d]	+4.3	3.48[a]	2.41[e]
HNO_3	−32.96	−32.10[b]	−0.9	3.35	2.17[g]
$MeNO_3$	−35.32	−29.05[d]	−6.3	4.06	2.85[h]
$EtNO_3$	−39.89	−36.83[d]	−3.1	4.69	2.91[f]
$MeNO_2$	−12.38	−12.19[i]	−0.2	4.84	3.46[j]
$EtNO_2$	−18.95	−23.54[i]	+4.6	5.36	3.58[f]
n-$PrNO_2$	−24.10	−29.68[i]	+5.6	5.75	
i-$PrNO_2$	−26.94	−33.90[i]	+7.0	5.63	
n-$BuNO_2$	−29.24	−34.42[i]	+5.2	6.14	
i-$BuNO_2$	−32.02	−39.13[i]	+7.1	5.62	

[a] Calculations are for *trans* isomer. [b] JANAF Thermochemical Tables, Dow Chemical Co., Midland, Mich., 1965. [c] P. Cox and R. L. Kuczkowski, *J. Am. Chem. Soc.*, **88**, 5071 (1966). [d] P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959). [e] P. Gray and M. J. Pearson, *Trans. Faraday Soc.*, **59**, 347 (1963). [f] Landolt-Börnstein, "Zahlenwerte and Funktionen," Part I, Springer Verlag, Berlin, 1951. [g] A. P. Cox and J. M. Riveros, *J. Chem. Phys.*, **42**, 3106 (1965). [h] N. V. S. Sidgwick, G. G. Hampson, and R. J. B. Marsden, "A Table of Dipole Moments," Gurney and Jackson Press, London, 1934. [i] D. E. Holcomb and C. L. Dorsey, *Ind. Eng. Chem.*, **41**, 2788 (1949). [j] E. Tannenbaum, R. J. Myers, and W. D. Gwinn, *J. Chem. Phys.*, **25**, 42 (1956).

The last two columns of Table II compare dipole moments calculated by the method of part V[3b] with experimental values. As in the cases studied previously, the MINDO method gives values which are systematically too large. There is, however, a good linear relation between the calculated and observed

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(7) L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," Chemical Society Special Publications, No. 11 and 18, The Chemical Society, London, 1958 and 1965.

(8) Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Part VI/2, George Thieme Verlag, Stuttgart, 1963, p 334.

Table III. Ionization Energies (eV) of Nitroalkanes, Alkyl Nitrites, and Methyl Nitrate

Molecule	I_1[a]	I_1[b]	I_1[c]	I_i $(i > 1)$[b]	I_i $(i > 1)$[c]
A. Nitromethane	11.08	11.23	11.93	(11.80), 14.22, (14.67), 15.42, 17.23, (17.49), (19.55)	11.98, 12.35, 13.76, 13.94, 14.92, 15.22, 15.55, 21.00, 27.00, 31.13, 37.45
B. Nitroethane	10.88	10.92	11.57	(11.55), 12.93, (13.70), 16.78, (17.34), 17.91, (19.41)	11.75, 12.12, 12.73, 13.03, 13.82, 14.09, 14.58, 15.30, 15.75, 20.18, 23.28, 29.52, 30.93, 37.32
C. 1-Nitropropane	10.81	10.75	11.29	(10.95), 12.23, 14.44, 16.75, (17.06), (19.44)	11.62, 11.98, 12.41, 12.61, 12.74, 13.42, 13.97, 14.36, 14.68, 14.94, 16.14, 20.08, 21.49, 25.33, 30.76, 31.28, 37.23
D. 2-Nitropropane	10.71	10.77	11.37	(10.94), 12.44, (14.41), 16.42, (19.15)	11.61, 11.97, 11.99, 12.52, 13.61, 13.73, 13.75, 14.01, 14.70, 15.00, 15.75, 19.30, 22.65, 25.10, 30.65, 31.03, 37.32
E. 1-Nitrobutane		10.71	11.03	(11.02), 13.51, (13.79), 16.80, 18.14, (19.42)	11.53, 11.89, 12.05, 12.30, 12.58, 12.88, 12.94, 13.72, 14.07, 14.51, 14.69, 14.86, 16.36, 20.01, 20.62, 23.01, 27.23, 30.69, 32.24, 37.15
F. 2-Nitrobutane		10.71	11.29	11.87, 13.74, (14.34), (14.78), 16.71, 17.51, 18.08	11.36, 11.55, 11.91, 12.31, 12.66, 12.80, 13.57, 13.86, 13.93, 14.25, 14.50, 14.93, 15.91, 19.19, 21.64, 22.88, 27.33, 30.71, 31.67, 37.36
G. Methyl nitrite			11.45		12.03, 12.68, 13.32, 13.88, 14.46, 14.86, 15.13, 21.57, 23.64, 32.87, 36.75
H. Ethyl nitrite		10.53	11.28	12.52, (12.83), (14.43), (15.61), (16.78), (19.26)	11.46, 12.26, 12.34, 12.78, 13.78, 13.86, 14.34, 14.89, 15.26, 20.46, 21.75, 27.26, 33.06, 36.68
I. 1-Propyl nitrite		10.34	11.04	(10.60), 11.86, (12.24), 14.28, (16.55), (19.28), (19.74)	11.34, 11.81, 12.11, 12.35, 12.88, 13.16, 13.75, 14.18, 14.37, 14.81, 15.60, 20.00, 21.44, 23.13, 29.57, 33.20, 36.64
J. 2-Propyl nitrite		10.23	10.93	(10.50), 12.04, (12.40), (14.74), (15.63), (19.24)	11.22, 11.89, 12.11, 12.34, 13.10, 13.40, 13.74, 14.11, 14.39, 14.42, 15.34, 19.23, 21.62, 24.46, 28.40, 33.39, 36.69
K. Methyl nitrate		11.53	12.59	(11.79), (12.44), 14.20, 15.58, (15.94), 18.08	12.71, 12.88, 13.06, 13.64, 13.89, 14.72, 15.17, 15.80, 16.16, 21.45, 24.35, 31.73, 33.56, 38.45

[a] Photoionization values of Watanabe, *et al.*[9] [b] This paper. [c] MINDO orbital energies.

values (Figure 2), the deviations being almost all within the possible limits of experimental error in the measured moments; one can therefore get quite good estimates of dipole moments by equating them to two-thirds of the MINDO values.

Ionization Potentials. According to Koopmans' theorem, the ionization potentials of a molecule should be approximately equal to its calculated SCF orbital energies; this relation has been shown[4] to hold closely for a number of hydrocarbons, and molecules containing carbon, hydrogen, nitrogen, and oxygen, when the orbital energies are calculated by the MINDO method. Table III shows a similar comparison for the compounds studied here. Only four of the compounds had been studied previously by methods other than electron impact; these values, determined by photoionization spectroscopy by Watanabe and his collaborators,[9] are also listed in Table III. The first three columns list values corresponding to the first ionization potentials (I_1), while the last two columns give the remaining ionization potentials derived from our photoelectron spectra, together with the MINDO orbital energies.[10] No measurements are reported for methyl nitrite since it proved too corrosive, attacking the metal diaphragm of the sample inlet valve.

As can be seen from Table III, our photoelectron values for I_1 are only in fair agreement with the photoionization values of Watanabe, *et al.*;[9] this is surprising, because in all previous cases the two methods have been found[4] to agree to within 0.03 eV. Since nitro compounds are labile to uv light, it is possible that the photoionization values may have been affected by the presence of photochemically produced impurities; effects of this kind are much less likely in the case of photoelectron measurements since here the incident

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(9) K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectry. Radiative Transfer*, 2, 369 (1962).

(10) Only potentials less than 21.22 eV are listed since this is the limit of a photoelectron spectrometer using helium resonance radiation as the light source.

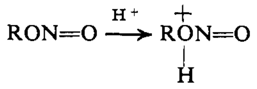
quanta are of such high energy that there is no danger of excitation to bound states with finite lifetimes, liable to undergo internal conversion.

The photoelectron values for I_1 are in good agreement with the calculated orbital energies; only in one case is there an inversion of order (*i.e.*, 1-nitrobutane and 1-propyl nitrite), and the numerical values in all cases agree to a few tenths of an electron volt. This provides a useful confirmation of the parameters used here (eq 1) for NO interactions. As usual,[4] the orbital energies are systematically greater than the measured ionization potentials; this would be expected, since Koopmans' theorem, being based on first-order perturbation theory, fails to allow for reorganization of orbitals or molecular geometry on passing from a molecule to its ion.

The resolution of our spectra is insufficient to allow useful comparisons to be made between the higher ionization potentials and orbital energies; the two sets of values are, however, consistent with one another, given that the orbital energies are expected to be systematically greater than the corresponding ionization energies and that our spectrometer cannot resolve ionizations differing by much less than 0.5 eV. Thus in the case of methyl nitrate, one has the following correlation (ionization potentials in eV, followed by corresponding orbital energies in parentheses); 11.53 (12.59); 11.79 (12.71, 12.88, 13.06); 12.44 (13.64, 13.89); 14.20 (14.72, 15.17); 15.58 (15.80); 15.94 (16.16); 18.08 (21.45).

Protonation of Nitrites and Nitrates

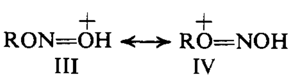
The protonation of compounds such as nitrous or nitric acids, or their esters, presents an interesting problem in that there are two different kinds of oxygen to which the proton might attach itself; see I, II, and III. Intuition based on resonance theory, or HMO theory, might lead one to expect protonation to occur at the doubly bound oxygen on the grounds that one can then write two more or less equivalent resonance structures for the resulting cation (*cf.* III with IV), or that the parent compound (*e.g.*, I) should be isoconjugate with an allyl anion and so should have the formal charge distribution indicated in V. The same problem of course also arises in the case of the corresponding nitrates (see VI, VII, and VIII). On the other hand the ease with which strong acids convert nitrites and nitrates to the ions NO^+ or NO_2^+ could be better explained if protonation gives the ions II or VII which could dissociate directly into water or an alcohol and the ion NO^+ or NO_2^+.



$$\mathrm{RON{=}O} \xrightarrow{H^+} \mathrm{R\overset{+}{O}N{=}O}$$

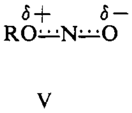
I II

or

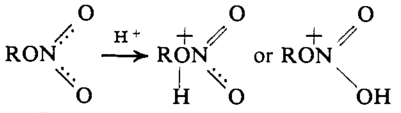


$$\mathrm{RON{=}\overset{+}{O}H} \longleftrightarrow \mathrm{R\overset{+}{O}{=}NOH}$$

III IV



V



VI VII VIII

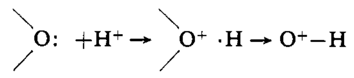
Table IV shows heats of formation for the two types of ion, calculated by the MINDO method. It will be seen that in all cases the ion is predicted to have the structure II or VII, an unexpected result but one clearly in good agreement with the chemical evidence. Admittedly the calculations refer to the gas phase and take no account of possible differences in energy of solvation; however, the calculated differences between the two forms of each ion are large enough (~10 kcal/mol for II/III, 20 kcal/mol for VII/VIII) to make it unlikely that solvation could make III or VIII the more stable.

Table IV. Heats of Formation of Protonated Nitrites and Nitrates

Parent compd	R	Heat of formation, kcal/mol II or VII	III or VIII	ΔH,[a] kcal/mol
I	H	+157.9	+167.5	−17.7
	CH_3	+147.2	+156.7	−1.4
	C_2H_5	+135.6	+146.7	+6.1
VI	H	+165.6	+186.2	+31.1
	CH_3	+150.5	+170.6	+41.3
	C_2H_5	+138.8	+159.1	+49.4

[a] Heat of reaction for eq 7.

The conclusion that II and VII are the preferred forms of the ions is not in fact as surprising as it may seem at first sight. It is true that III and VIII should have larger resonance energies, but there is another very important factor operating in the opposite direction. The protonation process can be regarded as formation of a dative bond between oxygen and H^+; from the following dissection



$$\mathrm{>O{:}} + H^+ \rightarrow \mathrm{>O^+{\cdot}H} \rightarrow \mathrm{O^+{-}H} \quad (5)$$

one can see that the corresponding over-all change in energy (ΔE) should be given approximately by

$$\Delta E = -E_{\mathrm{OH}} + I_{\mathrm{O}} - I_{\mathrm{H}} \quad (6)$$

where E_{OH} is the bond energy of the OH bond, I_{O} the valence state ionization potential of oxygen, and I_{H} the ionization potential of hydrogen. Now the orbital used by oxygen in formation II or VII is probably approximately of sp^3 type[11] while that in III or VIII is sp^2; the valence-state ionization potential is greater in the latter case by 2.3 eV or 53 kcal/mol.[14] Although the difference will be less than this in practice, since the OH bond will not be symmetrical and since the oxygen atom in II or VII will have a hybridization intermediate between sp^3 and sp^2, one might nevertheless expect this effect of hybridization to outweigh any differences in resonance energy, as between II and III or VII and VIII.

The same effect should of course operate in other analogous situations; the azines provide a good illustration. All methods of calculation predict that the nitrogen atom in pyridine should have a larger formal negative charge than that in an aliphatic amine; other things being equal, pyridine should then be a stronger

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(11) These compounds are isoelectronic with amides; the nitrogen atoms in formamide[12] and cyanamide[13] are known to be pyramidal.

(12) C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960).

(13) D. J. Miller, G. Topping, and D. R. Lide, *J. Mol. Spectry.*, **8**, 153 (1962).

(14) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

base than a saturated analog, *e.g.*, piperidine. In fact it is much weaker. This apparent anomaly can again be attributed to the different states of hybridization of the two types of nitrogen, sp^2 in pyridine and sp^3 in piperidine.

The results in Table IV can also be used to estimate the heats of dissociation (ΔH) of the ions II or VII into water, or an alcohol, and NO^+ or NO_2^+, *i.e.*

$$\begin{aligned} \mathrm{II} &\longrightarrow \mathrm{ROH} + \mathrm{NO}^+ \\ \mathrm{VII} &\longrightarrow \mathrm{ROH} + \mathrm{NO_2}^+ \end{aligned} \qquad (7)$$

The heat of formation of NO_2^+ has been measured[15] but not that of NO^+; we calculated the latter by the MINDO method, using the experimental value (1.0619 Å[16]) for the bond length. The values are given in (8).

$$\begin{aligned} \mathrm{NO}^+ &= +197.96 \text{ kcal/mol} \\ \mathrm{NO_2}^+ &= 244.5 \text{ kcal/mol} \end{aligned} \qquad (8)$$

Using these values together with the heats of formation in Table IV, and the heats of formation calculated previously[3b] for water, methanol, and ethanol, we arrive at the values of ΔH shown in the last column of Table IV.

It will be seen that the values of ΔH for II are negative, or small and positive, implying that II should dissociate very readily; this of course is the case, nitrous acid derivatives readily giving NO^+ with no evidence for the formation of stable protonated intermediates. The values of ΔH for VII are quite large and positive; the nitracidium ion is known as a stable species in solution, and dissociation to NO_2^+ occurs only under conditions where the resulting water is immediately protonated, this protonation helping to displace the equilibrium toward NO_2^+.

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

(16) E. Meischer, *Can. J. Phys.*, **33**, 355 (1955).

Vinyl Ether Hydrolysis. Specific Acid Catalyzed Hydrolysis of 4-Methoxy-3-buten-2-one[1]

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Abstract: The hydrolysis of 4-methoxy-3-buten-2-one (**1**) to 3-ketobutanal in aqueous solution is specific acid catalyzed and is further characterized by $k_2(D_2O)/k_2(H_2O) = 2.08$ and $\Delta S^{\ddagger} = -26.0 \pm 1.7$ eu. These results are consonant with an A2 mechanism involving rate-determining hydrolysis of the conjugate acid of **1**.

The hydrolysis of vinyl ethers (eq 1) is general acid catalyzed and exhibits a deuterium solvent isotope effect $k(D_2O)/k(H_2O) < 1$,[3-7] results in accord with a mechanism involving rate-determining proton transfer from the catalyst to the olefin. The present study is concerned with the hydrolysis of a substituted vinyl ether, 4-methoxy-3-buten-2-one (**1**), a reaction which formally involves olefin hydration of an α,β-unsaturated ketone and which proceeds *via* a mechanism exhibiting specific acid catalysis only.

$$\mathrm{R'OCH{=}CHR} + \mathrm{H_2O} \xrightarrow{k_{\mathrm{HA}}} \mathrm{RCH_2CHO} + \mathrm{R'OH} \qquad (1)$$

$$\underset{\mathbf{1}}{\mathrm{CH_3OCH{=}CHCOCH_3}}$$

Experimental Section

Reagents. Certified ACS grade inorganic salts were purchased from Fisher Scientific Co. Tap distilled water was redistilled through a Corning AG-1a still before use. 4-Methoxy-3-buten-2-one, bp 60° (6 mm) (lit.[8] 172°) was purchased from Aldrich Chemical Co., Inc. The pmr spectrum in $CDCl_3$ (TMS) showed singlets at δ 2.17 (CH_3CO), 3.72 (CH_3O), and doublets at 5.58 (OC=CH–) and 7.60 (OCH=C), J = 13 cps. Deuterium oxide, 99.8 atom % D, and DCl in D_2O were purchased from Diaprep, Inc. and from Ciba Corp.

Apparatus. Gilford Model 2000 and Beckman DBG spectrophotometers were used for the collection of rate data and for scanning reactions. Temperature was maintained in the cuvettes by circulating water of constant temperature from a Tamson T9 bath through thermospacers. pH was measured using a Radiometer PHM 22 pH meter with a PHA scale expander and a GK2021B combination electrode.

Kinetics. The course of the reaction of 4-methoxy-3-buten-2-one (**1**) was monitored at 250 mμ (ϵ 6.82 × 10^3) by following the loss of absorbance *vs.* time. All reactions were carried out in water at some specified temperature ±0.1° and at a calculated ionic strength of 1.0 *M* with KCl. The pH of each solution was determined before and after all runs and pH remained constant (±0.02 pH units) during all runs. ₸ cuvettes (3 ml) were filled to the stopper level with the appropriate HCl–KCl buffer or carboxylic acid–carboxylate salt buffer, capped, and allowed to come to thermal equilibrium. Reactions were started by adding a known amount of **1** in methanol *via* a micropipet to the appropriate solu-

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