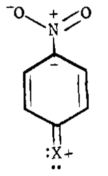
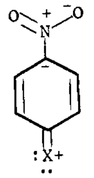
The nitro group is unique; based upon NQDR and NMR results it appears that the NO_2 group withdraws a constant amount of electron density from the ring regardless of what substituent is attached to the meta or para position. To further emphasize the unique electron-withdrawing properties of the nitro group, we focus our attention on the N–O vs. C–O bond order. Since force constants are related to bond order, we anticipate a linear correlation of IR stretching frequencies with Hammett σ values.[8] For substituted benzaldehydes and acetophenones this is observed.[3c] In contrast, the nitro asymmetric stretch correlates poorly with the Hammett σ values, and the symmetric stretching frequency is completely invariant to substitution.[9]

To better understand the nitro group's electron-withdrawing ability, we have carried out several ab initio molecular orbital calculations with an STO-3G basis set.[10] Total electron densities (Mulliken population analysis) and the corresponding π component (in parentheses) are summarized in Chart I. It is apparent that the charge density on oxygen and nitrogen is independent of substituent. Even the π-electron density, which by invoking canonical structure **1a** should show a large change, is likewise invariant to substituent.

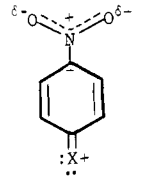
All of the available evidence points to the conclusion that the electronic environment of oxygen in nitrobenzene derivatives does not depend on meta and para substituents. We conclude that the nitro group withdraws a constant amount of electron density from the benzene ring whether the ring is electron rich or electron deficient. Consequently resonance structure **1a**, considered by many as a major contributor to the nitrobenzene resonance hybrid,[11] is not a valid structure for the description of para-substituent lone-pair delocalization. Instead, we invoke valence bond structure **5** to describe the chemical and physical properties of nitrobenzenes.



4



4a



5

The salient feature of **5** is that the nitro group resonance is not disrupted. The NO_2 group has two stable and energetically degenerate valence bond structures, **4** and **4a**. The loss of the NO_2 resonance more than offsets the system's drive to use **1a** in the molecular wave function.

Valence bond structure **5** is consistent with the physical characteristics of substituted nitrobenzenes. It allows for para-substituent lone-pair delocalization into the ring and accounts for the typically large dipole moments. Further, it explains the peculiarities observed in the IR stretching frequencies and ^{17}O NMR chemical shifts. Finally, it clarifies the NQDR results (the most sensitive and direct probe of electron density).

Because the nitrogen is directly attached to the carbanionic center, the electron density around the nitrogen atom will vary with the substituent's ability to localize charge at the point of NO_2 attachment. This is simply an inductive effect, not a mesomeric affect. Hence, a plot of *ehqQ* for nitrogen should, and does, correlate with σ.[6] The oxygens, since they are shielded from the carbanionic center by the nitrogen, are oblivious to the degree of negative charge buildup, and consequently *ehqQ* for oxygen is independent of σ.[6]

Invoking resonance structure **1a** localizes two negative charges near one another and disrupts the NO_2 group resonance. Our conclusion, contrary to popular belief, is that valence bond structure **1a** is not a major contributor to the molecular wave function of neutral nitrobenzenes and that **5** is.[12]

Acknowledgment. We thank Dr. C. P. Cheng for bringing the NQDR results to our attention. We also thank the Indiana University Bloomington staff for making their NMR spectrometer available to us and acknowledge the Indiana University Computer Network for generous use of their facilities.

Registry No. Nitrobenzene, 98-95-3; *p*-fluoronitrobenzene, 350-46-9; *p*-chloronitrobenzene, 100-00-5; *m*-chloronitrobenzene, 121-73-3; *p*-nitroanisole, 100-17-4; *m*-dinitrobenzene, 99-65-0; *m*-nitrobenzaldehyde, 99-61-6; *m*-nitrotoluene, 99-08-1; *p*-nitrotoluene, 99-99-0; *sym*-trinitrobenzene, 99-35-4.

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(8) For leading references of LFER's for aromatic systems with infrared spectral data see: (a) Rao, C. N. R. "Chemical Applications of Infra Red Spectroscopy"; Academic Press: New York, 1963. (b) Katritzky, A. R.; Topsom, R. D. "Advances in Linear Free Energy Relations"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: London, 1972. (c) Brownlee, R. T. C.; Topsom, R. D. *Spectrochim. Acta* **1975**, *31A*, 1677. (d) Brownlee, R. T. C.; DiStefano, J.; Topsom, R. D. *Ibid.* **1975**, *31A*, 1685.

(9) There appears to be a lack of agreement on whether or not ν_{sym} correlates with the Hammett substituent parameter. Also, the nature of the interactions giving rise to the nitro IR shifts has yet to be firmly established. Pertinent references: (a) Brown, J. F., Jr. *J. Am. Chem. Soc.* **1955**, *77*, 6341. (b) Kross, R. D.; Fassel, V. A. *Ibid.* **1956**, *78*, 4225. (c) Brownlee, R. T. C.; Cameron, D. G.; Topsom, R. D.; Katritzky, A. R.; Pozharsky, A. F. *J. Chem. Soc., Perkin 2* **1974**, 247. (d) Exner, O.; Kovac, S.; Solcaniova, E. *Collect. Czech. Chem. Commun.* **1972**, *37*, 2156.

(10) The molecular orbital calculations were performed with PHANTOM by D. Goutier, R. Macaulay, and A. J. Duke, *QCPE* **1974**, No 241, Indiana University, Bloomington, IN. Standard bond lengths and bond angles were used. The Dacre–Elder formalism was adapted with C_1–C_4 defining the plane of symmetry. Oscillations in the SCF part were damped with a weighting factor of 0.50 for the new density matrix.

(11) See for example: Wiberg, K. B. "Physical Organic Chemistry"; Wiley: New York, 1964; p 288. Hine, J. "Physical Organic Chemistry", 2nd ed.; McGraw Hill: New York, 1962; p 88. Hirsch, J. A. "Concepts in Theoretical Organic Chemistry"; Allyn and Bacon: Boston, 1974; p 101. Lowry, T. H.; Richardson, T. H. "Mechanism and Theory in Organic Chemistry"; Harper and Row: New York, 1976; p 64.

(12) The only molecule for which resonance structure **1a** has been seriously proposed is *p*-nitrophenolate. We would like to include in Table I *p*-nitrophenol and the corresponding anion. However, the ionized species, unlike the neutral phenol, is insoluble in most solvent systems we tried. Furthermore, even if the natural abundance ^{17}O chemical shift could be obtained, we would be uncertain of the contributions from contact ion pairing. Our conclusions unfortunately are limited to neutral species only.

Heats of Formation of the Ionic and Neutral Enols of Acetaldehyde and Acetone

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Received November 13, 1981

Theoretical[1,2] and experimental[3,4] results are in agreement that the enol radical cations of acetaldehyde and acetone are much more stable thermodynamically than their corresponding keto forms. This is in marked contrast to the neutral tautomeric pairs, in which the keto forms are generally more stable. Recently reported values for heats of formation, ΔH_f, and ionization energies, IE, for the ions and their neutral counterparts are given in Table I. Although the ΔH_f (neutral) and IE results for the enol of acetaldehyde (vinyl alcohol) are in reasonable agreement, the estimated IE values[7-9] for the enol of acetone show a wide

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(1) Bouma, W. J.; Poppinger, D.; Radom, L. *J. Am. Chem. Soc.* **1977**, *99*, 6443.

(2) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1979**, *101*, 5540.

(3) Holmes, J. L.; Terlouw, J. K.; Lossing F. P. *J. Phys. Chem.* **1976**, *80*, 2860.

(4) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1980**, *102*, 1591.

(5) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data Suppl. No. 1*, **1977**, *6*.

(6) Cox, J. F.; Pilcher, D. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

(7) Murad, E.; Inghram, M. G. *J. Chem. Phys.* **1964**, *40*, 3263.

(8) Meyerson, S.; McCollum, J. D. *Adv. Anal. Chem. Instr.* **1963**, *2*, 191.

(9) Bentley, T. W.; Johnstone, R. A. W. *Adv. Phys. Org. Chem.* **1970**, *8*, 242.

(10) Pollack, S. K.; Hehre, W. J.; *J. Am. Chem. Soc.* **1977**, *99*, 4845. Hehre (private communication) has remeasured $\Delta H_f[CH_2{=}C(OH)CH_3]$ and now reports it to be 44 ± 2 kcal mol^{-1}.

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Table I. ΔH_f and IE for Keto and Enol Radical Cations and Neutrals

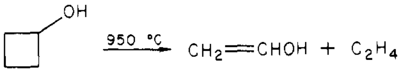
species	ΔH_f(ion), kcal mol^{-1}	ΔH_f(neutral), kcal mol^{-1}		ionization energy, eV	
		lit.	this work	lit.	this work
CH_3CHO	196	−39.7[6]		10.23[5]	
$CH_2{=}CHOH$	183.5[2]	−28.0[2]		(9.17)[2] [a]	
	181[3]	−26.5[3]	−29.8[b]	(9.0)[3] [a]	9.14
CH_3COCH_3	172	−51.9[6]		9.70[5]	
$CH_2{=}C(OH)CH_3$	158[4]	−38[10]	−38[b]	8.2[7]	8.48
				9.1–9.4[8]	
				8.75[9]	

[a] From ΔH_f(ion) − ΔH_f(neutral). [b] From ΔH_f(ion) − IE.

variance; ΔH_f for the neutral enol of acetone derived from these estimates and the value of 158 kcal mol^{-1} for ΔH_f of $[CH_2{=}C(CH_3)OH]^{+\cdot}$, with the relationship ΔH_f(neutral) = ΔH_f(ion) − IE, will of course show the same uncertainty. A direct experimental measurement of the IE of these two enols would permit more reliable values for the heats of formation of the neutral molecules to be obtained.

Vinyl alcohol is a transient species in the gas phase; it has been prepared[11] by the pyrolysis of ethylene glycol in a quartz tube at 1000 °C. The half-life was about 30 min. The apparent ease with which gas-phase vinyl alcohol rearranged to acetaldehyde in spite of a calculated activation energy barrier of 85 kcal mol^{-1} has been commented upon.[1] We report here a better pyrolytic source for vinyl alcohol and one for the enol of acetone, together with ionization energies measured by impact of a monoenergetic electron beam.[12]

Almost complete pyrolysis of cyclobutanol to vinyl alcohol plus ethene was obtained at 950 °C and 10^{-3} torr in a tubular quartz furnace[13] which leads directly into the ionization chamber.



The threshold for the ionization efficiency curve for m/z 44 (C_2H_4O) was 9.14 ± 0.05 eV. The cross section for ionization was quite small over the initital portion of the curve, suggesting that the Franck–Condon factors for the adiabatic transition are small. As pointed out by Bouma et al.,[2] the hydroxyl hydrogen in the lowest energy configuration of the ion is anti, in contrast with the syn position in the neutral molecule. A low probability for the adiabatic transition is therefore possible. The observed IE, 9.14 eV, is close to the 9.17-eV value derived in the theoretical study,[1,2] but the agreement is partly fortuitous because our experimental ΔH_f(vinyl alcohol)$^{+\cdot}$ from dissociative ionizations[3] is 2.5 kcal mol^{-1} lower than the value of 183.5 kcal mol^{-1} from the theoretical calculations. Our experimental IE, taken with ΔH_f(ion) = 181 kcal mol^{-1}, leads to $\Delta H_f[CH_2{=}CHOH]$ = −29.8 kcal mol^{-1}, with a probable error of ±2 kcal mol^{-1}.

The neutral enol of acetone, $CH_2{=}C(CH_3)OH$, was obtained in good yield from the pyrolysis of 1-methylcyclobutanol at 950 °C in the same apparatus. The threshold for the ionization efficiency curve for m/z 58 was 8.48 ± 0.05 eV. At temperatures above 950 °C the yield of enol decreased and ketene and methane were produced. From the ΔH_f for the enol of acetone,[4] 158 kcal mol^{-1}, and the experimental IE for the enol, 8.48 eV, ΔH_f[neutral $CH_2{=}C(CH_3)OH$] = −38 kcal mol^{-1}. This is identical with the value obtained by Pollack and Hehre[10] from ion cyclotron resonance experiments.

It is noteworthy that the substitution of CH_3 for H in vinyl alcohol decreases the ΔH_f(neutral) by 8.2 kcal mol^{-1}. The corresponding substitution for the isoelectronic species $CH_3CH{=}CH_2$ to give $(CH_3)_2C{=}CH_2$ decreases ΔH_f by a similar amount,[6] 9.1 kcal mol^{-1}. It is possible to derive from these results a useful new additivity term in the thermochemical scheme of Benson et al.,[14] for the group $O{-}(C_d)(H)$. Combining the presently accepted additivity terms [$C{-}(H)_3(C)$ = −10.08, $C_d{-}(H_2)$ = 6.26, $C_d{-}(O)(H)$ = 8.6, and $C_d{-}(O)(C)$ = 10.3 kcal mol^{-1}] with the heats of formation for neutral vinyl alcohol and for the enol of acetone reported above yields values for this additivity term of −44.7 and −44.5 kcal mol^{-1}, respectively. The satisfactory agreement between these figures leads us to propose the adoption of $O{-}(C_d)(H)$ = −44.6 ± 2 kcal mol^{-1}. With use of this term heats of formation of other enols may now be calculated.

Registry No. CH_3CHO radical cation, 36505-03-0; $CH_2{=}CHOH$, 557-75-5; $CH_2{=}CHOH$ radical cation, 57239-63-1; CH_3COCH_3 radical cation, 34484-11-2; $CH_2{=}C(OH)CH_3$, 29456-04-0; $CH_2{=}C(OH)CH_3$ radical cation, 34507-14-7.

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(11) Saito, S. *Chem. Phys. Lett.* **1976**, *42*, 399.

(12) Maeda, J.; Semeluk, G. P.; Lossing, F. P. *Int. J. Mass Spectrom. Ion Phys.* **1968**, *1*, 395. Lossing, F. P.; Traeger, J. C. *Ibid.* **1976**, *19*, 9.

(13) Lossing, F. P.; de Sousa, J. B. *J. Am. Chem. Soc.* **1959**, *81*, 281.

(14) Benson, S. W.; Cruikshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

Use of D-[$^{13}C_6$]Glucose Together with ^{13}C-Depleted Glucose and Homonuclear ^{13}C Decoupling To Identify the Labeling Pattern by This Precursor of the "*m*-C_7N" Unit of Geldanamycin

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Received December 30, 1981

A "*m*-C_7N unit", consisting of a benzenoid ring plus one carbon atom and a nitrogen attached meta to each other, has recently been identified as a metabolic unit in a number of antibiotics including pactamycin,[1] geldanamycin,[2] mitomycin,[3] porfiromycin,[4] rifamycin,[5] and actamycin[6] and is presumably found in a number of related compounds[7] such as maytansine and streptovaricin.[8]

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(1) (a) Rinehart, K. L., Jr.; Potgieter, M.; Delaware, D. L.; Seto, H. *J. Am. Chem. Soc.* **1981**, *103*, 2099–2101. (b) Weller, D. D.; Rinehart, K. L., Jr. *Ibid.* **1978**, *100*, 6757–6760.

(2) (a) Haber, A.; Johnson, R. D.; Rinehart, K. L., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 3541–3544. (b) Johnson, R. D.; Haber, A.; Rinehart, K. L., Jr. *Ibid.* **1974**, *96*, 3316–3317.

(3) (a) Hornemann, U.; Eggert, J. H.; Honor, D. P. *J. Chem. Soc., Chem. Commun.* **1980**, 11–13. (b) Hornemann, U. In "Antibiotics. IV. Biosynthesis"; Corcoran, J. W., Ed.; Springer-Verlag: Berlin, 1981; pp 295–312. (c) Hornemann, U.; Kehrer, J. P.; Numez, C. S.; Ranieri, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 320–322.

(4) Anderson, M. G. Kibby, J. J.; Rickards, R. W.; Rothschild, J. M. *J. Chem. Soc., Chem. Commun.* **1980**, 1277–1278.

(5) (a) Ghisalba, O.; Nüesch, J. *J. Antibiot.* **1981**, *34*, 64–71. (b) White, R. J.; Martinelli, E.; Gallo, G. G.; Lancini, G.; Beynon, P. *Nature* (*London*) **1973**, *243*, 273–277. (c) White, R. J.; Martinelli, E. *FEBS Lett.* **1974**, *49*, 233–236.

(6) Kibby, J. J.; McDonald, I. A.; Rickards, R. W. *J. Chem. Soc., Chem. Commun.* **1980**, 768–769.

(7) Rinehart, K. L., Jr.; Shield, L. S. *Fortschr. Chem. Org. Naturst.* **1976**, *33*, 231–307. The most recent addition to the group is apparently ansatrienin (Damberg, M.; Russ, P.; Zeeck, A., submitted for publication).

0002-7863/82/1504-2649$01.25/0