

Average Ionization Energies of Fragments in Molecules from Fragment Transfer Energies

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A method is described to determine the changes in the stabilities of fragments X and Y that result from the formation or cleavage of the X-Y bond. Fragment transfer energies are defined as the differences between the energies of the free fragments and of the fragment in the molecule. The sum of these transfer energies equals the bond dissociation energy, and they allow one to discuss the relation between fragment energies and bond stabilities. The method is illustrated by considering a reaction of the type $(X-Y)^+ \rightarrow X^+ + Y$ and, specifically, the dediazonium reactions of a wide variety of diazonium ions. X-N bonding in the diazonium ions results because the X^+ cations are more stabilized than the N_2 groups are destabilized by the charge transfer associated with bond formation, that is, cations force N_2 to form diazonium ions. The N_2 transfer energies are found to be correlated with the N_2 charges supporting the generally made assumption that fragment stabilities might be discussed in terms of fragment charges. The correlation is well approximated by a linear function and its slope defines the average ionization energy of a fragment in a molecule. It is found that the average ionization energy of N_2 in the diazonium ions roughly equals the ionization energy of free N_2 , and consequences are discussed.

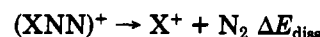
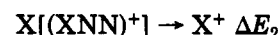
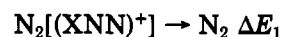
Introduction

Bond dissociation energies for homolytic dissociations $X-Y \rightarrow X\cdot + \cdot Y$ and heterolytic dissociations $X-Y \rightarrow X^+ + Y^-$ are important for the estimation of reaction energies. A wide variety of bond dissociation energies for homolytic dissociations are available,¹ and those values for the heterolytic reactions can be determined with the additional knowledge of the electron affinities and the ionization energies of the fragments. While bond dissociation energies measure the overall stabilization of the fragments X and Y upon bond formation, they do not contain information about the individual stabilizations of the fragments. In fact, the latter aspect of bond formation has received very little attention. In this article, we address the question of how bond formation affects the energies of the bonding fragments for a specific heterolytic dissociation reaction of the type $(X-Y)^+ \rightarrow X^+ + Y$. Fragment transfer energies are defined for this purpose, and a method is described for their determination. Results are reported of a theoretical analysis of the dediazonium reactions $(X-NN)^+ \rightarrow X^+ + N_2$. Both the dissociation energies and the fragment transfer energies have been determined, and their relation is discussed. Moreover, this reaction is advantageous for the present task as the associations of N_2 with the various X^+ cations occur with significantly different degrees of charge transfer depending on the nature of X. For the N_2 fragment, it is therefore possible to examine how its transfer energies are related to the charge transfer. This analysis leads to the definition of an average ionization energy of dinitrogen in a molecule. Its value is found to equal the ionization energy of free N_2 , and consequences and possible implications are discussed.

Fragment Transfer Energies

In a *Gedanken* experiment,² the reaction energies for the dediazonium reactions can be decomposed into the energy differences ΔE_1 between the N_2 group in the diazonium ion and free N_2 and into the energy differences ΔE_2 between the free cations and the X fragments in the

diazonium ions. In the equations defining the transfer energies, the notation F[M] is used to refer to the fragment



F in the molecule M. This Gedanken experiment allows one to study the origins of the X-N bond strengths since the energy associated with the bond formation results from the energies associated with the transfer of the free fragments into the molecule. We will refer to energy values ΔE_1 and ΔE_2 as fragment transfer energies. Positive transfer energies ΔE_1 and ΔE_2 would mean that bond dissociation destabilizes both fragments. The sum of the transfer energies equals the bond dissociation energy ΔE_{diss} .

The energies of the diazonium ions, of N_2 , and of the free cations X^+ can be determined directly with ab initio methods. For the determination of the energies of the fragments in the molecules, we have used Bader's theory of atoms in molecules.^{3,4} This theory is based on a partitioning of the molecular electron density distribution into atomic regions, the basins, by means of properties of the gradient vector field of the electron density. With this partitioning, it is possible to determine a variety of properties for the atomic basins that include populations and kinetic energies. The latter are of particular interest for the present discussion. Bader has shown that the virial theorem ($V = -2T$) holds not only for the iteratively determined molecular SCF Hartree-Fock wave functions, but also for each of the atomic basins. Since it is possible to determine atom kinetic energies by numerical integration within the basins, this theorem allows one to determine atom stabilities via $E = -T$. The transfer energies ΔE_1 can thus be determined from the N atom stabilities and the total energy of N_2 , and the transfer energies ΔE_2 can be determined similarly via the atom stabilities of the X fragment in the diazonium ion and the energy of the free X^+ cation. All of these computations were carried out at the RHF/6-31G* level⁵ of theory.

(1) (a) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper & Row: New York, 1981; p 147ff. (b) Isaacs, N. S. *Physical Organic Chemistry*; John Wiley: New York, 1987; p 36ff. (c) *Handbook of Chemistry and Physics*, 66th ed.; CRC Press: Boca Raton, FL, 1985; p F-174ff.

(2) *Gedanken* (German) experiment: intellectual, hypothetical, or imagined experiment. Literally: thought experiment.

(3) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Oxford University Press: New York, 1990.

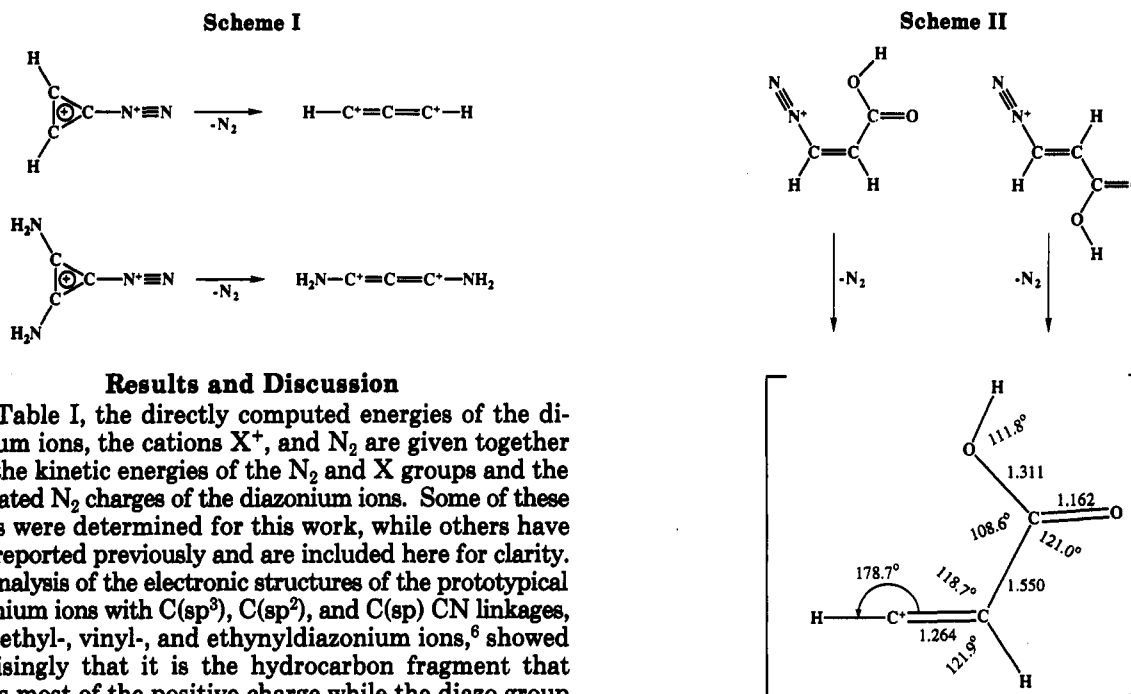
(4) Reviews: Bader, R. F. W. *Chem. Rev.* 1991, 91, 893. (b) Bader, R. F. W. *Acc. Chem. Res.* 1985, 18, 9. (c) Bader, R. F. W.; Nguyen-Dang, T. T.; Tal, Y. *Rep. Prog. Phys.* 1981, 44, 893.

(5) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley: New York, 1986.

Table I. Integrated N_2 Charges, Total Energies, and Integrated Fragment Stabilities^a

	SCF energies ^b		integrated properties		
	$E(X-NN^+)$	$E(X^+)$	$IC(N_2)^c$	$T(N_2)^d$	$T(X)^d$
FNN ⁺	207.83103	98.63261	1.055	108.31858	99.50681
HONN ⁺	183.91622	74.83022	0.736	108.58549	75.33292
H ₂ NNN ⁺	164.15343	55.12729	0.372	108.82624	55.32719
H ₃ CNN ⁺	148.21606	39.23064	0.161	108.88118	39.33485
H ₅ C ₂ NN ⁺	187.26441	78.31123 ^e	0.158	108.81823	78.44618 ^f
H ₃ C ₂ NN ⁺	186.05935	77.08673	0.077	108.93511	77.12443
HC ₂ NN ⁺	184.79772	75.78555	-0.007	109.01516	75.78200 ^f
CPD	222.75854	113.69863 ^h	0.223	108.79089	113.96764
DACPD	332.95769	224.02156 ^h	0.117	108.88338	224.07737
<i>cis</i> -CVD	373.66402	264.68999	0.087	108.93578	
<i>trans</i> -CVD	373.66398	264.68999	0.072	108.92873	
PhNN ⁺	338.74309	229.75839	0.018	108.92150	229.82115

^aAll values are based on RHF/6-31G* wave functions. ^bTotal energies ($-E$) in atomic units. $E(N_2, \text{RHF}/6-31G^*) = -108.94395$ au. ^cIntegrated charges of the N_2 group in the $(XNN)^+$ ions. ^dIntegrated kinetic energies of the N_2 and X fragments in $(XNN)^+$ in atomic units. ^eClassical structure. The C_{2v} structure is 1.19 kcal/mol less stable at that level. ^fN atoms were integrated, and $T(X)$ was determined by difference. ^gNote that the entry C1+PA for this molecule in ref 6 actually gives the values for C2+PA. ^hEnergies of the ring-opened didehydrided allene and diaminoallene dications.



Results and Discussion

In Table I, the directly computed energies of the diazonium ions, the cations X^+ , and N_2 are given together with the kinetic energies of the N_2 and X groups and the integrated N_2 charges of the diazonium ions. Some of these values were determined for this work, while others have been reported previously and are included here for clarity. The analysis of the electronic structures of the prototypical diazonium ions with $C(sp^3)$, $C(sp^2)$, and $C(sp)$ CN linkages, the methyl-, vinyl-, and ethynyldiazonium ions,⁶ showed surprisingly that it is the hydrocarbon fragment that carries most of the positive charge while the diazo group is strongly polarized but carries only a small charge. We proposed a new bonding model that is consistent with the electron density distributions that also applies to diazonium dications⁷ (Scheme I) such as cyclopropeniumyldiazonium dication (CPD) and its 2,3-diamino derivative (DACPD), and to aromatic diazonium ions,⁸ all of which are included in the analysis presented here. We have recently reported on neighboring group interactions in β -carboxyvinlyldiazonium ions⁹ (CVD) and *cis*- and *trans*-3-diazonium propenoic acid (Scheme II) are included here as representatives. Larger N_2 charges occur in heterosubstituted diazonium ions such as FNN⁺, HONN⁺, and H₂NNN⁺.¹⁰ For the methyl and ethyldiazonium ions, we have confirmed the bonding model with electron density analyses at correlated levels,¹¹ and atom stabilities were reported that were determined at the RHF/6-31G* level

Table II. Transfer Energies ΔE_1 and ΔE_2 , and Dediazoniation Energies^a

	ΔE_1	ΔE_2	ΔE_{diss}		
			$\Delta E_1 + \Delta E_2$	direct	diff
FNN ⁺	-392.43	548.57	156.14	159.68	3.54
HONN ⁺	-224.94	315.45	90.51	89.13	-1.38
H ₂ NNN ⁺	-73.86	125.44	51.58	51.58	0.00
H ₃ CNN ⁺	-39.39	65.39	26.00	26.02	0.02
H ₅ C ₂ NN ⁺	-78.89	84.68	5.79	5.79	0.00
H ₃ C ₂ NN ⁺	-5.55	23.66	18.11	17.99	-0.12
HC ₂ NN ⁺	44.68	-2.23	42.46	42.81	0.35
CPD	-96.05 ^b	168.81 ^c	72.76	72.77	0.01
DACPD	-38.01	35.02 ^c	-2.99	-4.91	-1.92
<i>cis</i> -CVD	-5.13				
<i>trans</i> -CVD	-9.55				
PhNN ⁺	-14.09	39.39	25.30	25.57	0.27

^aValues are based on the RHF/6-31G* wavefunctions and given in kcal/mol. ^bThis value was erroneously given as -96.38 kcal/mol in ref 7. ^cNote that the ΔE_2 values in ref 7 were determined as the differences between ΔE_1 and the dissociation energy.

but with the MP2(full)/6-31G* structures. For consistency, ethyldiazonium ion was now also analyzed at the RHF/6-31G* level with the structure optimal at that level (Table I). Note that all of these diazonium ions are known

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(9) Glaser, R.; Horan, C. J.; Nelson, E.; Hall, M. K. *J. Org. Chem.*, in press.(10) (a) Glaser, R.; Choy, G. S.-C. *J. Phys. Chem.* 1991, 95, 7682. (b) Glaser, R.; Choy, G. S.-C. Manuscript in preparation.(11) Glaser, R.; Choy, G. S.-C.; Hall, M. K. *J. Am. Chem. Soc.* 1991, 113, 1109.

and have been characterized.¹²⁻¹⁴

Transfer energies ΔE_1 and ΔE_2 are given in Table II together with the dissociation energies ΔE_{diss} . The two values of ΔE_{diss} in this table were determined as the sum of the transfer energies or directly from the total energies of the diazonium ions and their fragments, respectively. The differences between these values give an estimate of numerical inaccuracies in the determination of the kinetic energies of the fragments and, as can be seen, the differences are rather small and without consequences for the conclusions.

In the case of the cyclopropenyldiazonium ions, the ΔE_2 values refer to the ring-opened cations as shown in Scheme I. For the ethynyldiazonium ion, the dissociation energy and the associated ΔE_2 value were determined with reference to the $^3\Pi$ ground state of the ethynyl cation.¹⁵ The gas-phase dediazonation reactions of the parent vinyldiazonium ion as well as of the ethyldiazonium ions lead to nonclassical bridged cations at electron-correlated levels while computations at the RHF level would indicate classical cation structures. The ΔE_2 values of these systems are affected by this electron correlation effect on the cation structures to a small extent, while the corresponding ΔE_1 values are not affected since the ΔE_1 values depend only on the energies of the diazonium ions and free N_2 . For the diazonium ions, correlation effects do not result in significantly different structures. The β -carboxyvinyl cation that would formally result from dediazonation of the 3-diazonium propenoic acid isomers was optimized at the RHF/6-31G* level in C_s symmetry and vibrational frequency computation showed the resulting structure to be a minimum. The structure is shown in Scheme II. However, this vinyl cation structure does no longer correspond to a stationary structure on the potential energy surface when correlation effects are included at the second-order Møller-Plesset level. For the carboxyvinyl diazonium ions, values for $T(X)$, ΔE_2 , and ΔE_{diss} have therefore been omitted.

N_2 Charge and Transfer Energy. The transfer energies ΔE_1 are found to be negative; that is, the N_2 groups are destabilized in the diazonium ions compared to free N_2 , and this destabilization increases as the electronegativity of X increases. A positive ΔE_1 value is found only for the ethynyldiazonium ion, the only molecule in which the integrated N_2 charge is slightly negative.

Atom and fragment charges often are discussed with the implied assumption that the charges are correlated with the fragment energies. With the ΔE_1 energies and the N_2 group charges, we can test the validity of this assumption. In particular, the selection of the wide variety of diazonium ions allows one to study this dependence in more quantitative terms. In Figure 1, a plot is shown of the transfer energies ΔE_1 versus the N_2 group charges for the diazonium ions. The transfer energies are found to be correlated in a linear fashion with the N_2 group charge with a negative slope and a nonzero positive intercept. The positive intercept accounts for the stabilization of the overall neutral N_2 group in the electric field of the cation as a result of polarization. The slope is negative; a decreasing N_2 pop-

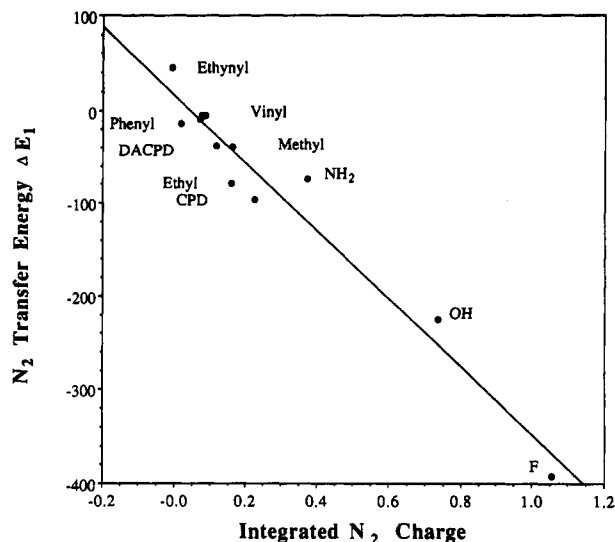


Figure 1. Destabilization of the diazo group in diazonium ions is correlated with its integrated charge. ΔE_1 is the relative energy of the diazo group with regard to free N_2 in kcal/mol.

ulation reduces the N_2 stability. The finding that the correlation is well approximated by a linear function supports the usually made assumption that the stabilities of fragments can be discussed in terms of their charges. While this assumption holds for the class of diazonium ions, in discussions of selected representatives of this class other factors may also play important roles (vide infra).

The slope and the intercept of the regression line are affected by electron correlation in significantly different ways. The absolute values of the transfer energies may show significant correlation effects because the electronic structures of free N_2 and of the bonded N_2 in the diazonium ion are rather different.¹⁶ The differences between the transfer energies ΔE_1 , however, are much less affected since they reflect only the differences between different diazonium ions. Relative values of transfer energies should thus be affected little. Consequently, electron correlation is likely to affect the intercept to some extent but to have comparatively little effect on the slope.

The linear regression function is well described by eq 1. The slope of this function specifies the change in the

$$\Delta E_1 = -363.69(q(N_2)) + 15.246 \quad (R^2 = 0.954) \quad (1)$$

transfer energy ΔE_1 with increasing N_2 charge, and it has the dimension of energy/charge. The slope represents nothing else but the negative average ionization energy of dinitrogen in a molecule; about 364 kcal/mol. How does this value compare with the ionization energy of free N_2 itself?

The determination of the ionization energy of N_2 requires the consideration of the radical cation N_2^+ ($^2\Sigma_g^+$) and demands higher theoretical levels. In Table III, directly computed values for the adiabatic ionization energy of N_2 are listed for various theoretical levels including annihilation of spin contaminants in the UHF reference¹⁷ of the radical cation. While the computed bond length of 1.133 Å of N_2^+ at the highest correlated level compares well with the experimental value¹⁸ of 1.116 Å, the adiabatic ionization energies determined at the Møller-Plesset levels, re-

(12) Nonaromatic diazonium ions. (a) Laali, K.; Olah, G. A. *Rev. Chem. Intermediates* 1985, 6, 237. (b) Ferguson, E. F. *Chem. Phys. Lett.* 1989, 156, 319. (c) Olah, G. A.; Herges, R.; Laali, K.; Segal, G. A. *J. Am. Chem. Soc.* 1986, 108, 2054.

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(15) (a) Glaser, R. *J. Am. Chem. Soc.* 1987, 109, 4237. (b) Hanack, M.; Vermehren, J.; Helwig, R.; Glaser, R. *Stud. Org. Chem.* (Amsterdam) 1987, 31, 17.

(16) For discussions of correlation effects on dediazonation energies, see ref 11 and references cited therein.

(17) Schlegel, H. B. *J. Chem. Phys.* 1986, 84, 4530.

(18) *International Tables of Selected Constants 17. Spectroscopic Data Relative to Diatomic Molecules*; Rosen, B., Ed.; Pergamon Press: London, 1970.

Table III. Adiabatic Ionization Energies of Dinitrogen^{a,b}
ionization energy $N_2 \rightarrow N_2^+ (^2\Sigma_g)$

theoretical model	annihilation ^c		
	none	s + 1	s + 1, s + 2
SCF	362.65 ^d	358.91	358.92
MP2(fc)	345.07 ^d	343.06	343.06
MP3(fc)	359.60	358.94	358.94
MP4(fc,sdtq)	344.74	344.08	344.08
MP2(full)	347.54 ^e		
MP2(fc)	347.37 ^e	345.04	345.05
MP3(fc)	362.34	361.52	361.53
MP4(fc,sdtq)	345.66	344.84	344.85
MP2(full)	350.09 ^f		
MP2(fc)	349.78 ^f	347.39	347.40
MP3(fc)	365.14	364.30	364.31
MP4(fc,sdtq)	348.52	347.68	347.68
CISD(fc)	359.49		
CISD(fc,acc)	355.72		

^a First four energies are based on the SCF/6-31G* structure, RHF for N_2 and UHF for the radical cation, next four entries on the MP2(full)/6-31+G* structures, and the last six entries on the MP2(full)/6-311+G(df) structures. Ionization energies are given in kcal/mol. Higher-order Moeller-Plesset and CISD calculations employed the frozen core approximation, MPx(fc). CISD energies are given without and with size consistency corrections (acc). S^2 values are given only if they differ more than 10^{-4} from 0.75. ^b Bond lengths in Å. Dinitrogen: 1.0784 at RHF/6-31G*, 1.1299 at MP2(full)/6-31+G*, and 1.1147 at MP2(full)/6-311+G(df). Radical cation: 1.0936 at UHF/6-31G*, 1.1466 at UMP2(full)/6-31+G*, and 1.1329 at MP2(full)/6-311+G(df). ^c The ionization energies were determined without and with annihilation of contributions from quartet (s + 1) or sextet (s + 2) states of the radical cation. The eigenvalues for the S^2 operator of the N_2^+ wavefunctions are given in footnotes d-f. ^d $S^2(0) = 0.766$ and $S^2(1) = 0.751$. ^e $S^2(0) = 0.769$. ^f $S^2(0) = 0.769$.

spectively, are somewhat less than the experimental ionization energy of 359.2 kcal/mol.¹⁹ The values determined at the SCF level agree surprisingly well with the experimental value, but this result is fortuitous as the Hartree-Fock limit value²⁰ is 368.7 kcal/mol. The CI value of 360.2 kcal/mol reported by Ermler and McLean²¹ and our CISD values agree well and are in good agreement with experiment. It thus appears that the ionization energy of N_2 in the molecule is roughly equal to the ionization energy of free N_2 .

The finding that the correlation is rather well approximated by a linear function is interesting in light of the fact that the ΔE_1 values reflect both the spatial characteristics of the basins and the electron density distribution therein whereas the N_2 charges reflect only the former. The intrinsically different qualities of these properties are of course the reason for the scattering about the correlation line. It is important to emphasize that it is for this reason that a meaningful value for the slope of the correlation can only be obtained if a wide variety of bonding situations is sampled. For small samples of related molecules, linear relations might indeed be obtained that might even show less scattering²² but in these cases the correlation would reflect—not average—the energetic effects caused by factors other than charge transfer. In other words, for the

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(20) Cade, P. E.; Sales, K. D.; Wahl, A. C. *J. Chem. Phys.* 1966, 44, 1973.

(21) Ermler, W. C.; McLean, A. D. *J. Chem. Phys.* 1980, 73, 2297.

(22) Aromatic systems CPD, DACPD and PhNN⁺: $\Delta E_1 = -401.54(q(N_2)) - 1.4658$ (eq 2.1; $R^2 = 0.954$). Methyl-, vinyl-, and ethynyldiazonium ions: $\Delta E_1 = -500.42(q(N_2)) + 38.445$ (eq 2.2; $R^2 = 0.987$). XNN⁺ with X = F, OH, NH₂: $\Delta E_1 = -465.23(q(N_2)) + 105.02$ (eq 2.3; $R^2 = 0.995$).

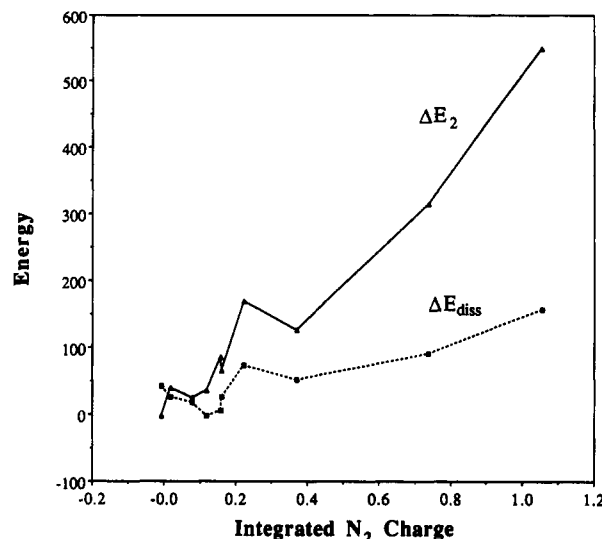


Figure 2. Transfer energies for the X fragments, ΔE_2 (triangles, solid line), and the dissociation energies, ΔE_{diss} (squares, dashed line), are plotted versus the integrated charges of the N_2 groups in the diazonium ions. The stabilization of the X fragments increases with increasing charge transfer, and it overcompensates the destabilization of the N_2 group.

class of diazonium ions we can state that the destabilization of the N_2 group is related with the N_2 charge via the ionization energy of the N_2 molecule but for individual representatives other factors also play important roles. For example, the charge transfers determined for methyl- and ethyldiazonium ions are rather similar but their fragment stabilizations do differ in a characteristic fashion as we have discussed elsewhere.²³

X Fragment Stabilization and X-N Bond Strength.

The cations are stabilized as the diazonium ions are formed; the ΔE_2 values are positive. In Figure 2, the transfer energies ΔE_2 and the dissociation energies ΔE_{diss} are plotted against the N_2 charges. In all cases, XN bond formation is exothermic because the X fragment is more stabilized than the N_2 fragment is destabilized. One might say that the cations force N_2 to form diazonium ions. The electron affinities of the X⁺ fragments in the molecules are larger than the ionization energies of the N_2 group in the corresponding diazonium ions. The bond strengths of the X-N linkages increase with the electronegativity of X since the stability of the diazo group decreases almost linearly with the reduction of the N_2 charge and because the stabilization of the X fragment increases with the electronegativity of X (electronegativity parallels electron affinity).

The discussion of the transfer energies ΔE_1 suggests that it might also be possible to relate the stabilization of an electron-enriched fragment in a molecule with the charge of that fragment in the molecule via the electron affinity of the free fragment. To pursue this question, analyses are required of a series of association reactions of an X⁺ cation or of a neutral X Lewis acids with a variety of different donor molecules Y and to determine the average electron affinity of X in molecules in the way described above for the determination of the average ionization energy of dinitrogen in molecules.

Conclusion

A fragment energy analysis of the dediazonation reactions of a representative variety of diazonium ions has been described to illustrate a method for the discussion of

(23) See ref 11 for a comparative analysis.

fragment stability changes associated with bond formation. The transfer energies for the N_2 fragments are found to be negative while the transfer energies of the X^+ cations are positive. Bonding in diazonium ions is achieved because the cations are stabilized more than the N_2 groups are destabilized and not because both fragments would benefit energetically from their association. The comparison of the heterosubstituted diazonium ions ($X = F, OH, NH_2$) with the RNN^+ ions shows that the XN bond stabilities largely depend on the charge transfer from N_2 onto X^+ . Increasing X electronegativity leads to larger charge transfer and—since the electron affinity is larger than the ionization energy of N_2 —to larger bond dissociation energies. Among the $(RNN)^+$ ions, the relation is more complicated and not solely determined by charge transfer.

The N_2 transfer energies are correlated with the N_2 charges in a way that is well approximated by a linear function. This finding supports the generally made assumption that fragment stabilities can be discussed by fragment charges. More importantly, the slope of the linear correlation between the N_2 charges and the transfer energies ΔE_1 defines an average ionization energy of N_2 in molecules. It is found that its value is roughly equal to the ionization energy of free N_2 . This finding suggests that the (de)stabilization of an electron-depleted fragment

in a molecule can be estimated via the determination of its charge in the molecule and with the knowledge of its ionization potential. Similarly, it might also be possible to relate the stabilization of an electron-enriched fragment in a molecule with its charge via the electron affinity of the free fragment. A method was outlined that allows one to test this hypothesis. Future research will have to examine the generality of these findings and it is hoped that the present work might stipulate such investigations.

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Registry No. CPD, 129523-44-0; DACPD, 129551-42-4; *cis*-CVD, 137946-13-5; *trans*-CVD, 137946-14-6; FNN^+ , 33687-51-3; $HONN^+$, 76412-54-9; H_2NHN^+ , 43422-90-8; H_3CNN^+ , 20404-06-2; $H_5C_2NN^+$, 84027-64-5; $H_3C_2NN^+$, 64709-62-2; HC_2NN^+ , 108561-02-0; $PhNN^+$, 2684-02-8; F^+ , 14701-13-4; HO^+ , 12259-29-9; H_2N^+ , 15194-15-7; H_3C^+ , 14531-53-4; $H_5C_2^+$, 14936-94-8; $H_3C_2^+$, 14604-48-9; HC_2^+ , 16456-59-0; Ph^+ , 17333-73-2; N_2 , 7727-37-9; 1,2-propadiene-1,3-diylium, 99818-38-9; 1,3-diamino-1,2-propadiene-1,3-diylium, 137964-66-0; 1-carboxyethenylum, 137946-15-7.

Notes

On the Origin of the C₃ Framework of Yeast-Generated (*R*)-*S*-Benzyl Thioglycerate

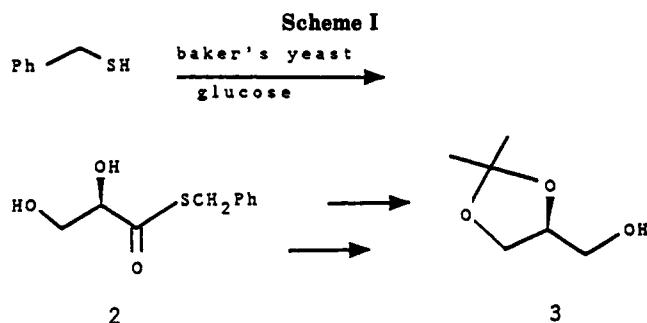
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While there is an established knowledge on the predictable behavior of baker's yeast as a stereoselective reducing agent,¹ numerous reports are dedicated to "new capacities" attributed to this microorganism, which are observed when unnatural substrates are treated with fermenting yeast.²

In this context, we recently reported³ on the formation of *S*-benzyl thioglycerate from baker's yeast (b.y.) incubation of benzyl mercaptan in the presence of glucose 1 as summarized in Scheme I. The product 2 of high optical purity was assigned the *R* absolute configuration, as proved by its conversion into isopropylidenglycerol (3) of *S* configuration and $\geq 98\%$ ee. Starting from 20 g of $PhCH_2SH$, 1.6 g of thioglycerate 2 was obtained, 14 g of



the mercaptan being recovered unreacted. Despite the modest chemical yield, we considered of interest the obtainment of a chiral compound in enantiomerically pure form which is available through a procedure similar to an extractive process from a natural source. In fact, the capture of a biosynthetic intermediate with a nonnatural reactant is of potential interest when the educt, as in the present case, is a highly functionalized chiral synthon complementary to those offered by nature as starting materials for the synthesis of chiral substances.⁴ Attempts to extend the reaction leading to the thioglycerate 2 to other thiols gave different products,⁵ thus suggesting that benzyl mercaptan is unique in its ability to be accepted in some metabolic transformation in yeast. We conceived that the product is obtained as the consequence of the action of benzyl mercaptan as a nucleophile in the glycolytic pathway of glucose. To obtain experimental support

(1) Servi, S. *Synthesis* 1990, 1.

(2) See, for instance: Gibbs, D. E.; Barnes, D. *Tetrahedron Lett.* 1990, 31, 5555. Rama Rao, K.; Bhanumathi, N.; Sattur, P. B. *Tetrahedron Lett.* 1990, 31, 3201. Fadnavis, N. W.; Deshpande, A.; Chauhan, S.; Bhalerao, U. T. *J. Chem. Soc., Chem. Commun.* 1990, 1548. Fronza, G.; Fuganti, C.; Grasselli, P.; Poli, G.; Servi, S. *J. Org. Chem.* 1988, 53, 6153. Buist, P. H.; Dallmann, H. G. *Tetrahedron Lett.* 1988, 29, 285.

(3) Fronza, G.; Fuganti, C.; Pedrocchi-Fantoni, G.; Servi, S. *Chem. Lett.* 1989, 12, 2141.

(4) Seebach, D.; Kalinowski, H. O. *Nachr. Chem. Techn.* 1976, 24, 415.

(5) Fuganti, C.; Pedrocchi-Fantoni, G.; Servi, S. *Agric. Biol. Chem.* 1991, 55.