along the helical axis appear to be minor in their effects upon the polarizability of this macromolecule. Although these results appear to be at variance with flow birefringence investigations on proteins and viruses in mixed solvents, these differences may be explainable in terms of anisotropic hydration and differential solvation in the latter. Since differential solvation effects may be less important in DNA,[52] it is clear that additional flow birefringence studies are required on low molecular weight DNA involving mixed solvents, and including the effects of the pH, ionic strength, and ionic size and nature. Such studies are currently in progress.

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Communications to the Editor

Rearrangements of Molecular Ions of Dialkyl-*N*-nitrosamines[1]

Sir:

We wish to report evidence for rearrangement of molecular ions of a series of dialkyl-*N*-nitrosamines. The occurrence of this rearrangement, which is analogous to the first step of the McLafferty rearrangement,[2] was suggested by the observation that the molecular ion, $R_2NNO\cdot^+$, undergoes an ion–molecule reaction (eq 1) in which a proton is transferred only when the

$$R_2NNO\cdot^+ + R_2'NNO \longrightarrow R_2'NNOH^+ + \text{products} \qquad (1)$$

neutral species $R_2'NNO$ is equally as basic as, or more basic than R_2NNO. The reaction is not observed when R_2NNO is less basic than $R_2'NNO$.

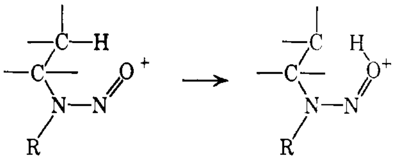
Ion cyclotron resonance (icr) techniques[3,4] were utilized to identify the occurrence of ion–molecule reactions. Observations on individual compounds and mixtures were made at a total pressure of 2×10^{-5} Torr, using a nominal ionization energy of 14 eV. In all mixtures, the single-resonance intensities of molecular ions were adjusted to an approximately 1 : 1 ratio.

Relative gas-phase basicities of substituted nitrosamines were established by observing proton transfer between one compound, $R_2'NNO$, and the conjugate acid of another, R_2NNOH^+ (eq 2).[5] The gas-phase

$$R_2NNOH^+ + R_2'NNO \longrightarrow R_2'NNOH^+ + R_2NNO \qquad (2)$$

results, where $Me_2NNO < Et_2NNO < n\text{-}Pr_2NNO < i\text{-}Pr_2NNO \approx n\text{-}Bu_2NNO$ is the observed order of base strengths, parallel those observed in solution.[6] Proton transfer occurred only from the conjugate acid of the weaker base to the stronger for all possible pairs except i-Pr_2NNO and n-Bu_2NNO, where the reaction was seen to proceed in either direction. n-Bu_2NNO was found to be of equal base strength as $EtNH_2$. Extrapolation of the data of Haney and Franklin[7] sets an upper limit of 214 ± 3 kcal/mol for the proton affinity of n-Bu_2NNO.

The specificity of reaction 1 is not readily explicable on the basis that $R_2'NNO$ directly abstracts a proton bonded to a carbon atom in the alkyl chain. Such a reaction would not be expected to depend upon the relative basicities of the proton acceptor and conjugate neutral base but rather on the availability of primary, secondary, or tertiary protons. On the other hand, proton abstraction from an O–H moiety, resulting from a rearrangement of the molecular ion (eq 3) prior to proton transfer, would be a reflection of relative basicities of the nitrosamines. Support for this argument is obtained from the observed loss of a fragment of 17 mass units in the mass spectra of ethyl-, n-propyl-, isopropyl, and n-butyl-*N*-nitrosamines; this fragment has been identified by high-resolution mass spectrometry as an OH radical. Identification of collision-induced fragmentation pathways[8] by icr double resonance indicates that m/e (M − 17) is coming only from the parent molecular ion. Dimethyl-*N*-nitrosamine molecular ion, which lacks the necessary hydrogen for a six-membered transition state for transfer of a hydrogen from carbon to oxygen, does not readily undergo loss of 17 mass units. However, transfer of a proton from carbon for the least basic member of the family is still feasible.



(3)

This rearrangement is analogous to a rearrangement postulated for nitropropane[9] on the basis of a M − 17 peak, but the icr evidence now suggests strongly that the loss of OH occurs from a rearranged molecular ion, not from a protonated form. The loss of OH from dialkylnitrosamines has been observed previously,[10] but its origin was previously unknown.

In the course of this study several other observations have been made. Single-resonance spectra of reaction pairs (obtained under the specified conditions) all show the ratio of $M\cdot^+$ to $(M + 1)^+$ to be greater than one for the less basic of the pair, while the protonated form

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[1] This work was performed under NSF Grant No. GP 7551.

[2] J. Diekman, J. MacLeod, C. Djerassi, and J. Baldeschwieler, *J. Amer. Chem. Soc.*, **91**, 2069 (1969).

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[4] J. Baldeschwieler, *Science*, **159**, 263 (1968).

[5] F. Lampe, J. Franklin, and F. Field, *Progr. React. Kinet.*, **1**, 67 (1961).

[6] W. Layne, H. H. Jaffé, and H. Zimmer, *J. Amer. Chem. Soc.*, **85**, 435 1816 (1963).

[7] M. Haney and J. Franklin, *J. Phys. Chem.*, 73, 4328 (1969).

[8] F. Kaplan, *J. Amer. Chem. Soc.*, **90**, 4483 (1968).

[9] N. M. M. Nisberring, T. J. de Boer, and H. J. Hofman, *Recl. Trav. Chim. Pays-Bas*, **84**, 481 (1965).

[10] J. Collin, *Bull. Soc. Roy. Sci. Liege*, **23**, 201 (1954).

of the more basic compound is always more intense than its parent species. Reactions 1 and 2 both show a negative dk/dE_{ion},[11] with the change being much greater for the latter reaction. Charge transfer (eq 4)

$$R_2NNO\cdot^+ + R_2'NNO \longrightarrow R_2NNO + R_2'NNO\cdot^+ \qquad (4)$$

proceeds irreversibly from the less basic to the more basic compound. This is in agreement with the expected decrease in ionization potential with increasing length or branching of the alkyl chain.

[11] J. Beauchamp and S. Buttrill, *J. Chem. Phys.*, **48**, 1783 (1968).

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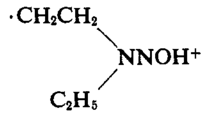
Electrical Effect of Free-Radical Groups[1]

Sir:

In the course of a study of dialkyl-*N*-nitrosamines by ion cyclotron resonance we have found a way to estimate the electrical (substituent) effect of groups like $\cdot CH_2CH_2^-$.

In a previous communication[2] we have shown that the order of base strengths in the gas phase of a series of compounds R_2NNO is R = Me < Et < *n*-Pr < *n*-Bu ≈ *i*-Pr. We have also shown that a rearrangement occurs in the parent ions of these compounds, leading to ions of the structure

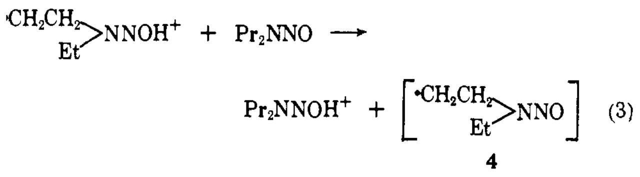


$$\left.\begin{matrix}\cdot CH_2CH_2\\ C_2H_5\end{matrix}\right\rangle NNOH^+$$

and that these ions undergo proton transfer with free nitrosamines. For diethyl-*N*-nitrosamine reactions 1–3

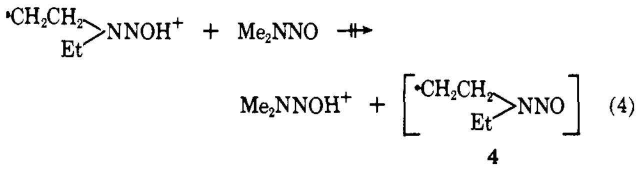
$$\underset{}{Me_2NNOH^+} + \underset{\mathbf{2}}{Et_2NNO} \not\rightleftarrows \underset{\mathbf{1}}{Me_2NNO} + Et_2NNOH^+ \qquad (1)$$

$$Et_2NNOH^+ + \underset{\mathbf{3}}{Pr_2NNO} \not\rightleftarrows \underset{\mathbf{2}}{Et_2NNO} + Pr_2NNOH^+ \qquad (2)$$



$$\left.\begin{matrix}\cdot CH_2CH_2\\ Et\end{matrix}\right\rangle NNOH^+ + Pr_2NNO \longrightarrow Pr_2NNOH^+ + \underset{\mathbf{4}}{\left[\left.\begin{matrix}\cdot CH_2CH_2\\ Et\end{matrix}\right\rangle NNO\right]} \qquad (3)$$

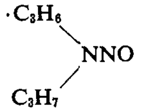
were observed, among others, but the reverse of reactions 1 and 2 and reaction 4 were shown not to occur.



$$\left.\begin{matrix}\cdot CH_2CH_2\\ Et\end{matrix}\right\rangle NNOH^+ + Me_2NNO \not\longrightarrow Me_2NNOH^+ + \underset{\mathbf{4}}{\left[\left.\begin{matrix}\cdot CH_2CH_2\\ Et\end{matrix}\right\rangle NNO\right]} \qquad (4)$$

Reactions 1 and 2 and their reverse show that the basicity sequence is **1** < **2** < **3**, as previously indicated. Reactions 3 and 4 further show that another basicity sequence is **1** < **4** < **3**. In other words, replacement of $-C_2H_5$ in **2** by $\cdot CH_2CH_2-$ to give **4** does not alter the basicity by more than the difference of the basicities between **1** and **2** or **2** and **3**.

The same arrangement can be made for the sequence **2**, **3**, Bu_2NNO (**5**), and **6**, where $-C_3H_6\cdot$ is *probably*



$$\left.\begin{matrix}\cdot C_3H_6\\ C_3H_7\end{matrix}\right\rangle NNO$$

6

$CH_3\dot{C}HCH_2-$, since this is the species formed by a δ hydrogen abstraction. The basicity sequences then are **2** < **3** < **5** and **2** < **6** < **5**. This shows that the electrical effects of $-C_2H_4\cdot$ and $-C_3H_6\cdot$ lie, respectively, between those of Me and Pr and Et and Bu. Since the difference between Me and Pr is small and that between Et and Bu even smaller, it may be concluded that the effects of $-C_2H_6\cdot$ and Et are very nearly the same, as are those of $-C_3H_7\cdot$ and Pr.

Similar information on $-CH_2\cdot$, $-C_4H_8\cdot$ (presumably $CH_3CH_2\dot{C}HCH_2-$), and *i*-$C_3H_6\cdot$ (presumably $H_2\dot{C}(CH_3)CH$) is not as complete. The reactions observed show that $\cdot CH_2-$ is less electron releasing than Et, but not how much less, and that the other two radical groups are more electron releasing than Pr, but not how much more. However, the conclusion suggests itself that each radical group has an electrical effect very nearly the same as that of the corresponding alkyl group.

Unfortunately, no information is available on the detailed structure of the free-radical groups. Although it was assumed that the radical site is β to the amino group, there is no way, at this time, to assure that no internal rearrangement shifting the site has occurred.

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Borohydride Reduction of σ-Bonded Organopalladium Complexes in the Norbornenyl–Nortricyclenyl System. Evidence against a Radical Mechanism

Sir:

Reductive cleavage of d^8 or d^{10} metal–carbon bonds by borohydride is well known, particularly among compounds of palladium, platinum, and mercury. We now report that in the norbornenyl–nortricyclenyl system, σ-bonded organopalladium complexes Ia and IIa are reduced by sodium borodeuteride with complete retention of stereochemistry, and with little rearrangement. By contrast, the mercury analogs of Ia and IIa are known to afford rearranged products from borohydride reduction, apparently *via* radical intermediates.[1]

In order to determine the stereochemistry and extent of deuterium substitution in the products by nmr, it was necessary to devise conditions for reduction which avoid hydrogenation of double bonds[2] and hydrogen-

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