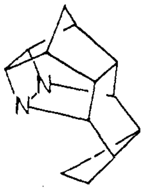
$5^{+\cdot}$ must be twisted as well as bent, and $\Delta E°\,'$ for **5** is sharply increased compared with that of **4**. The amount of twist attained cannot be determined without a knowledge of the amount of bend, but it is clear that twisting substantially destabilizes $5^{+\cdot}$.[9] For $6^{+\cdot}$, even more twisting is required (if N_2 is flat, the angle between the two orbitals on nitrogen bearing the three "nonbonding" electrons would be 90°), and the species is far less long-lived than other hydrazine radical cations. No reduction wave could be observed for $6^{+\cdot}$ in a cyclic voltammogram, even at rapid scan rate and low temperature (50 V/s at −50 °C). The hydrazine cation is so twisted that it behaves like an amine cation radical, and rapidly decomposes, presumably by deprotonation. The oxidation peak potential is +0.84 V vs SCE at 200 mV/s and 0.91 at 50 V/s, at room temperature. If the electron-transfer rate remains rapid relative to the scan rate, E_p^{ox} would be less positive than $E°\,'$, and $\Delta E°\,'$ would be >15 kcal/mol for **6**.

The caged hydrazine **8**[10] was prepared by catalytic hydrogenation of **9**, obtained by the method of Berning and Hünig.[11]



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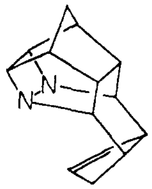

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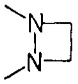

10

Its radical cation is not very long-lived, but $E°\,'$, could be determined at room temperature by cyclic voltammetry, and is the largest yet observed for a hydrazine with saturated alkyl substituents. The $\Delta E°\,'$ for **8**, at +13.8 kcal/mol, shows that $8^{+\cdot}$ is very destabilized compared with the less restricted diazetidine **10**. This destabilization is clearly a result of the nitrogens of $8^{+\cdot}$ not being able to flatten very much because of its caged structure. The nitrogen ESR splitting of $8^{+\cdot}$ is 26.8 G (−90 °C, butyronitrile, $(p\text{-BrC}_6\text{H}_4)_3\text{N}^+\text{SbCl}_6^-$ oxidation; $a(2\ \text{H}) = 8.4$ G), far larger than for **10**[3c] ($a(2\ \text{N}) = 15.0$ G) and indeed 8 G larger than for any other hydrazine radical cation yet studied.[3] Although bending a nitrogen a modest amount is not very destabilizing at all (as in **4**), requiring a great amount of bending seriously destabilizes a hydrazine radical cation (as in **8**). Great twisting of the radical cation is not only at least as costly in energy but makes the cation lifetime extremely short.

Acknowledgment. We thank the National Science Foundation for support of this work, both through research grants and the Major Instrument program.

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(5) (a) **4** was prepared from the corresponding bicyclic hydrazide[5b] by $LiAlH_4$ reduction followed by reductive methylation using $NaBH_3CN$, formaldehyde. The empirical formula was established by high resolution mass spectroscopy; spectral properties were consistent with assigned structure. (b) Mikhlina, E. E.; Komarova, N. A.; Rubstov, M. V. *Khim. Geterotsikl. Soedin., Akad, Nauk Latv. SSR* **1966**, 259; **1969**, 851.
(6) This assumes that the chair-chair form is the stablest, as it is in other bridgehead unsubstituted bicyclo[3.3.1]nonane derivatives which are not endo substituted at C_3 or C_7. Unfortunately, low-temperature ^{13}C NMR studies by W. C. Hollinsed have failed to define the conformations of **4**. Although conformational broadening of several of the lines is observed near −90 °C, and the temperature dependence of the chemical shifts before significant broadening is observed requires at least two conformations to be significantly populated, only a single eight-line pattern was observed at −130 °C, and we lack models to adequately assign the lines.
(7) Nelsen, S. F.; Buschek, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 6987.
(8) Lesko, P. M.; Turner, R. B. *J. Am. Chem. Soc.* **1968**, *90*, 6888.
(9) There is a modest negative increment in $\Delta E°\,'$ for **5** because of the flattening occurring in a five-membered ring, in contrast to that in the six-membered rings of **3** and **4**; see ref 2c. With its five-membered ring, **5** might be slightly strained relative to **3**, **4**, and **6**; this could slightly decrease $\Delta E°\,'$.
(10) **8** had mp 132–133 °C. The empirical formula was established by high resolution mass spectroscopy; spectral properties were consistent with assigned structure.
(11) W. Berning and S. Hünig, *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 777.

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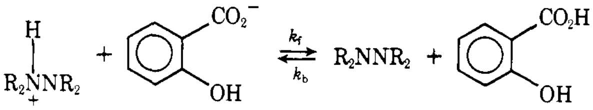
Anomalous Brønsted Behavior of the Proton-Transfer Equilibrium and Rate Constants for Tetraalkylhydrazines and Salicylic Acid

Sir:

Reaction 1 has been studied with several tetraalkylhydrazines in dimethyl sulfoxide containing 0.10 M tetraethylammonium perchlorate as supporting electrolyte. Values for $K = k_f/k_b$ were measured by potentiometric titration using a glass electrode (Ag/0.01 M $AgNO_3$ in Me_2SO as reference electrode) and those for k_f by a chronoamperometric technique developed by Evans and Kinlen[1] for this purpose. Data for the 13 hydrazines studied which have methyl and/or substituted methylene substituents are summarized in Table I. The order listed is that of decreasing log K (increasing basicity). The basicity of these hydrazines is seen to be rather sensitive to the nature of the alkyl substituents, K varying by five decades in this series. Lengthening the alkyl chains decreases basicity for the acyclic compounds (**1–6**) compared with that of tetramethylhydrazine (**7**). Tetraisobutylhydrazine was too feeble a base for measurement of log K by our method. The cyclic compounds **8–13** are more basic than **7**. The lone pair-lone pair dihedral angle, θ, of the unprotonated form may be of some importance in determining basicity. We note that **13**, which has $\theta \sim 0°$,[2] is ≥2.2 pK units more basic than the other compounds. Other factors are also clearly contributors.



(1)

The rate constants for proton transfer are also sensitive to structural changes in the alkyl substituents, k_f varying by 3.5 decades and k_b by 7.3 decades in the compounds studied. Two features of these rate data are remarkable. The first is that very slow rates of proton transfer are observed for these systems, despite the fact that proton transfer is occurring between oxygen and nitrogen, so that one might have anticipated these to be "normal" proton-transfer systems.[3] The rate constants quoted in Table I correspond to $\Delta G^{\ddagger}$ values varying between 7.5 and 17.4 kcal/mol. Slow proton transfers in dimethyl sulfoxide have been previously observed.[4] The second unusual feature of these systems is illustrated by the Brønsted plot of log k_f vs. log K shown in Figure 1. Considerable scatter from a straight line is observed; these compounds have not been chosen to minimize steric differences between them, but to provide a variety of equilibrium N–N rotation conformations. Nevertheless, it is clear that the plot has a negative slope (the least-squares line through **1–12** shown has $\alpha = -1.16$, correlation coefficient 0.92, average deviation 0.31 log units), requiring that the Brønsted plot for the reverse reaction, log k_b vs. log K^{-1}, has the slope $\beta = +2.16$ (same average deviation as for the foreward reaction, correlation coefficient 0.98). A

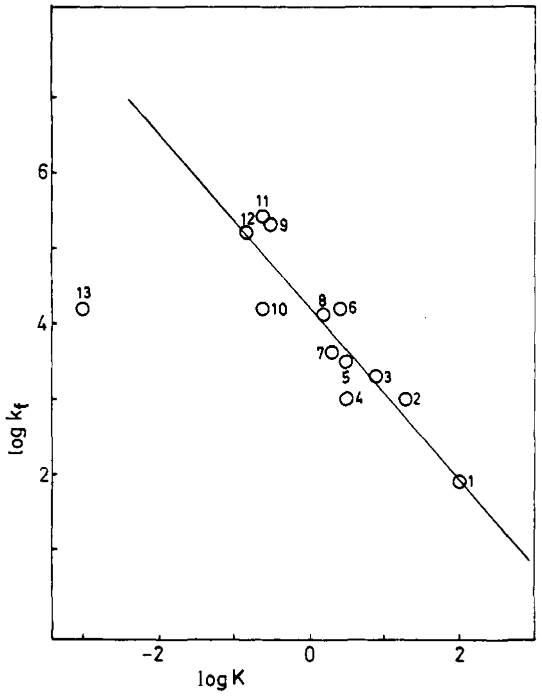
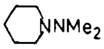
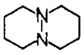
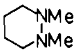
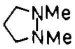
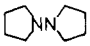
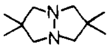


Figure 1. Brønsted plot for some tetraalkylhydrazine, salicylic acid proton transfers, log k_f vs. log K.

Table I. Equilibrium and Rate Constant Data for some Tetraalkylhydrazine Proton-Transfer Reactions with Salicylic Acid in Me_2SO[a]

no.	compd	log K	log k_f	log k_b
1	Pr_2NNPr_2	2.0	1.9	−0.1
2	*i*-BuMeNNMe-*i*-Bu	1.3	3.0	1.7
3	*n*-Bu_2NNMe_2	0.9	3.3	2.4
4	EtMeNNMeEt	0.5	3.0	2.5
5	Et_2NNEt_2	0.5	3.5	3.0
6	Et_2NNMe_2	0.4	4.2	3.8
7	Me_2NNMe_2	0.3	3.6	3.3
8		0.2	4.1	3.9
9		−0.5	5.3	5.8
10		−0.6	4.2	4.8
11		−0.6	5.4	6.0
12		−0.8	5.2	6.0
13		−3.0	4.2	7.2

[a] 25.0 °C; units of k_f and k_b are given in L mol^{-1} s^{-1}; estimated uncertainty in log K is ±0.1 unit; precision of determination of log k_f for **7** is ±0.1 unit.

qualitative description of what these results might indicate seems useful. Consider tetramethylhydrazine as the "parent" compound, from which differences are observed when the methyls are replaced by other alkyl groups. For illustration only, we make the crude assumption that the principal reason for observation of different $\Delta G°$ values for the other hydrazines lies in the free energy of the ions $HydH^+ + Sal^-$. This might be partially justified by pointing out that changes in the size and shape of the alkyl groups will change solvation stabilization, which ought to be far more important for ions than neutral compounds. Expressing this idea quantitatively, $G° = -0.4 + \Delta[G°(BH^+ + A^-)]$, since $\Delta G°$ for tetramethylhydrazine is −0.4 kcal/mol. To obtain the observed Brønsted behavior, effects that stabilize or destabilize the ions must have about the same magnitude of effect on the transition state for proton transfer. Because tetramethylhydrazine has $\Delta G_f^{\ddagger} = 12.3$ kcal/mol, if the effects were the same size, $\Delta G_f^{\ddagger} = 12.3 + \Delta[G°(BH^+ + A^-)]$. Energy diagrams using these assumptions are shown as Figure 2, and it is noted that k_b would show greater variation with $\Delta G°$ than would k_f. A Brønsted plot would have $\alpha = -1$, $\beta = +2$, approximately the behavior observed. Although this model is certainly oversimplified (as pointed out below, assuming $\Delta G° = \Delta[G°(BH^+ + A^-)]$ is unrealistic because of conformational effects on hydrazine stability), it illustrates that very unusual behavior must be occurring to give the observed plots.

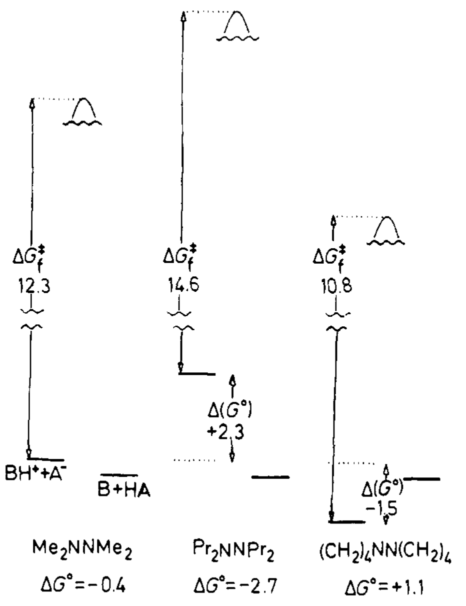


Figure 2. Energy diagrams for **7**, **1**, and **12** using the assumptions in the text.

As Kresge[5] has recently emphasized, such "anomalous" Brønsted exponents, in which α and β do not lie between 0 and 1, are rare. The only major exception to normal behavior previously reported is nitroalkane deprotonation-reprotonation.[5,6] Breakdowns of the Leffler Principle, Hammond's Postulate, and Marcus rate theory all must occur for observation of anomalous Brønsted exponents,[5] making the reasons for such behavior of considerable interest. For the nitroalkane cases, Kresge in his review[5] rationalizes the anomalous behavior by postulating that the charge distribution in the transition state for deprotonation (most of the negative charge at carbon, little π C=N bond character) is quite different from that of the product nitronate anion (most negative charge at oxygen, complete π C=N character). Bordwell and coworkers[6] have recently placed these concepts on a more structural basis by obtaining evidence for a pyramidal carbanion as at least a "pseudo intermediate". More than one type of alkyl interaction in a system is necessary for obtaining anomalous Brønsted behavior.[5,6] The case of hydrazines is fundamentally different from that of nitro compounds, because both the protonated and neutral forms are expected to have nearly tetrahedral nitrogens. Rehybridization at nitrogen upon deprotonation cannot be of major significance, as rehybridization at carbon clearly is in the nitroalkane case. Instead, we suggest that the structural reason for anomalous Brønsted behavior of these hydrazines is most likely to be rotation about the N-N bond. It is clear from considerable conformational work[7,8] that requiring coplanar nitrogen lone pairs leads to electronic destabilization of a neutral hydrazine. If protonation of the hydrazine "turned off" this electronic destabilization (and it might well even lead to electronic stabilization for coplanar $^+$NH bond and remaining lone pair), a rationalization for the anomalous Brønsted behavior could be provided, since steric and electronic interactions are considerably different in gauche and coplanar lone-pair conformations. Work designed to test these ideas is in progress.[9]

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(1) (a) Evans, D. H.; Kinlen, P. J., unpublished work. (b) Kinlen, P. J., Ph.D. Thesis, University of Wisconsin, 1978. (c) The potential was stepped from a value where hydrazine is not oxidized to one where electron transfer is diffusion controlled, and the kinetic current (i_K) monitored as a function of time, comparing its value in the presence of an excess of acid, where the hydrazine is effectively all protonated, with the diffusion current (i_D) measured in the absence of acid. The presence of an oxidation wave attributed to the Hyd$^{+}\cdot$,A$^-$ ion pair precluded the use of usual pseudo-first-order deprotonation conditions (and use of acetonitrile even in the absence of an excess of A$^-$). The heterogeneous equivalent technique of Ružić and Feldberg[1d] was used to calculate a theoretical curve for i_K/i_D (ref 1b, pp 82–93; computer program, pp 216–218) which was followed well experimentally. For tetramethylhydrazine, the experimental values of k_b thus determined were observed to be constant to ±0.1 log unit over a hydrazine concentration range of 1.0–4.8 mM and a salicyclic acid concentration range of 50–200 mM (ref 1b, pp 139–146). The sensitivity of the rate constants to the concentration of water in the Me_2SO has not been explicitly tested, but the Me_2SO samples employed (ref 1b, p 80) have a residual water concentration of ~10 mM. (d) Ružić, I; Feldberg, S. *J. Electroanal. Chem.* **1974,** *50*, 153.

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(6) Bordwell, F. G.; Bartmess, J. E.; Hautala, J. A. *J. Org. Chem.* **1978,** *43*, 3095, 3101, 3107, 3113, and references therein.

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(9) We thank the National Science Foundation for support of this work, under Grants CHE77-24627 and CHE78-08727.

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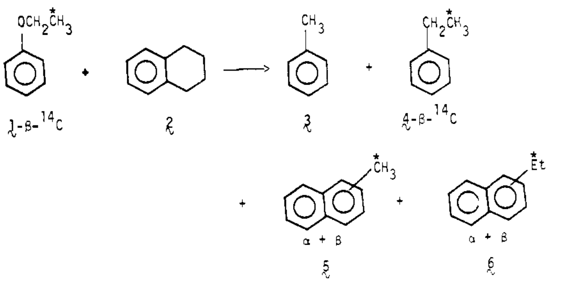
1,2 Shift of Phenyl from Oxygen to Carbon in a Free Radical[1]

Sir:

The importance of tetralin as a hydrogen donor in coal technology is well known,[2] and we recently reported on its reactions with Wyodak and with Illinois No. 6 vitrain, as well as with a series of model compounds.[3-5] We observed[4] that coal and tetralin-^{14}C when heated at 400 °C for 1 h yield traces of carbon-14-labeled α- and β-methylnaphthalenes. Since tetralin alone[5] yields no measurable amounts of methylnaphthalenes, we presume that the methyl groups in these compounds originate in the coal. Treatment of several aralkyl hydrocarbons and ethers with tetralin under the same conditions also yielded, among many other products, 4–10% methylnaphthalenes; experiments[4] with carbon-14-labeled hydrocarbons and ethers leave no doubt that intermolecular transfer of carbon occurs in the formation of the alkylnaphthalenes.

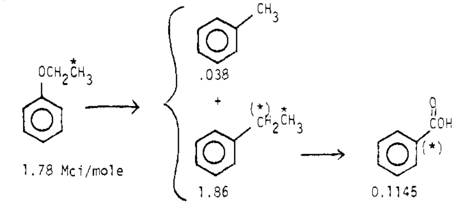
We report here on the reactions, with tetralin at 400 °C, of phenetole-α-^{14}C and phenetole-β-^{14}C.[6] In a typical run (18 h, 62% conversion) the yields, based on GC analyses were as follows: benzene, 11%; toluene, 11%; ethylbenzene, 11%; phenol, 47%; methylnaphthalenes, 16%; ethylnaphthalenes, 4%. Water was also formed. GC–MS analyses revealed[5] traces of other compounds. Monitoring of the radioactivity[7] of the toluene, ethylbenzene, and methyl- and ethylnaphthalenes from phenetole-α-^{14}C disclosed that these products contained carbon-14. An unexpected and surprising result from the reaction of phenetole-β-^{14}C (**1**-β-^{14}C) with tetralin (**2**) at 400 °C was the observation that the toluene (**3**) contained only a trace of carbon-14, whereas ethylbenzene (**4**) and the alkylnaphthalenes (**5** and **6**) were all labeled. The result for toluene was confirmed by its isolation and radioactivity assay.[8] The carbon-14 distribution in the ethylbenzene-^{14}C produced was determined after isolation by oxidation[9] to benzoic-^{14}C acid and carbon-14 determination.[8] The results are shown in Scheme I and were checked independently through similar experiments with phenetole-α-^{14}C.[10]



Although the alkylnaphthalenes (**5** and **6**) were formed through intermolecular reactions,[11] the mechanisms for the formation of **3** and **4** could, in principle, be either inter- or intramolecular. To resolve this question, we carried out the experiments outlined in Scheme II, in which a 50:50 mixture of phenetole-α-^{14}C and ethyl *p*-tolyl ether were heated with tetralin at 400 °C for 40 h. If toluene and ethylbenzene were formed by intramolecular processes, then only toluene and ethylbenzene should contain carbon-14, as shown in situation 1 in Scheme II. If the processes are intermolecular, then all four products should be labeled (2). The *p*-xylene and *p*-ethyltoluene produced were devoid[7] of radioactivity, signifying intramolecular processes.[12]

There are five conceivable pathways for the homolysis of phenetole; these yield the radical pairs A + B, C + D . . . J + K. Phenetole-β-^{14}C is portrayed to illustrate the carbon-14 distributions in the appropriate products (Scheme III). We recognize that C–H homolysis occurs through hydrogen ab-

Scheme I. Radioactivity Distributions in Toluene and Ethylbenzene Fractions Obtained from Heating Phenetole-β-^{14}C in Tetralin at 400 °C.



Scheme II. Results Expected for Crossover Reactions of Phenetole-α-^{14}C with ethyl *p*-tolyl ether in tetralin at 400 °C through intramolecular (1) or intermolecular (2) processes.