The Lack of an α Effect for Proton Abstraction from Carbon Acids

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Interest in the α effect remains unabated after 10 years of investigation and speculation.[3] The question of whether there is a kinetic α effect associated with proton abstraction by a nucleophile has not been satisfactorily answered. Methoxylamine and diethyl ketoxime exhibit large positive deviations from the Brønsted plot for general base catalysis of the hydrolysis of ethyl trifluorothiolacetate.[4] However, this deviation has been established to be due to a change in mechanism from general base catalysis of hydrolysis to nucleophilic attack for methoxylamine and diethyl ketoxime.[5] The α effect in general base catalyzed aminolysis is well known,[3,6] but finds ready explanation in the fact that the ester is undergoing simultaneous nucleophilic attack. Oximate anions have been shown to be considerably better catalysts than expected in reactions such as the dehydration of acetaldehyde hydrate[7] and the hydration of *s*-dichloroacetone;[8] however, explanations not involving the α effect have been suggested for these cases.[9,10] In particular, the solvents used for the reaction (91% acetone–water and 95% dioxane–water, respectively) were not those in which the pK_a's were obtained (water). The only quantitative approach to the question of the appearance of an α effect in proton abstraction from carbon is found in a study of the general base (amine) catalyzed ionization of nitroethane. The Brønsted β value for this reaction was found to be 0.5 and no α effect was observed with hydrazines. It was concluded from this study that general base proton removal from a carbon acid was not subject to the α effect. However, the factors leading to the kinetic α effect for hydrazine and peroxy anions are now known to differ,[11] and peroxy anion was not investigated with nitroethane. In addition, it has recently been shown, in the reaction of hydrazine with 17 substrates of assorted type, that a positive linear relationship exists between the magnitude of the α effect and the position of the transition state as determined by the Brønsted β value.[12] It would appear that our previous study with nitroethane is inconclusive because $\beta_{\max}$ values for nitroalkane ionization exceed 1.0, making β difficult to interpret[13] in terms of the position of the transition state along the reaction coordinant.

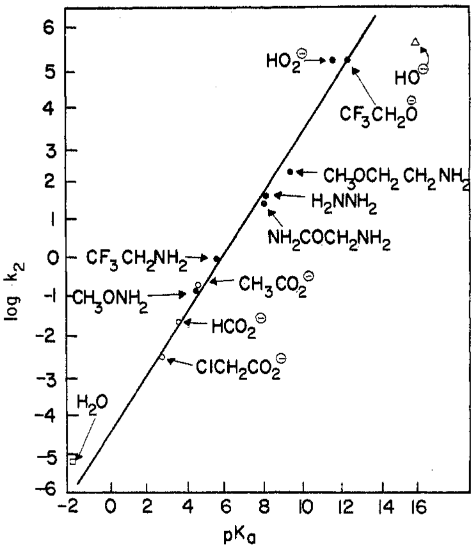

Figure 1.—Brønsted plot for the general base catalyzed detritiation of *tert*-butylmalononitrile-*1-t*. The points for water, hydroxide, and carboxylate ions are from ref 9.

Hibbert, Long, and Walters[14] have shown that the detritiation of *tert*-butylmalononitrile-*1-t* is a general base catalyzed reaction whose slow step is triton transfer from the cyanocarbon acid. They report a β value of *ca.* 0.9 derived from points for three carboxyl ions and a very small tritium kinetic isotope effect suggesting the transition state to be productlike. In addition, from their finding of an almost diffusion-controlled rate of reprotonation of the anion they suggest that in cyanocarbon acid anions far less delocalization of electrons occurs than in the case of the nitroalkanes.[15]

Having noted a positive correlation between the magnitude of the α effect and the Brønsted β[12] it occurred to us that proton (triton) abstraction from *tert*-butylmalononitrile with its β of *ca.* 0.9 would be an ideal reaction to provide a conclusive answer as to whether the α effect is operative when a carbon acid is the substrate. We have, therefore, studied the rates of detritiation of *tert*-butylmalononitrile-*1-t* in suitable α-effector and non-α-effector buffers employing the experimental procedure of Long, *et al.*[14,16] The second-order rate constants for triton abstraction (Table I) are plotted *vs.* the pK_a of the conjugate acid of the nucleophile in the Brønsted fashion in Figure 1. Included in Figure 1 are the experimental results reported from Long's laboratory.[14] The straight line of Figure 1 (slope 0.8) is the least squares line through all points regardless of base type except those for water and hydroxide ion. It is clear from Figure 1 that no significant α effect is present with methoxylamine, hydrazine, or peroxide anion. The values of $k_{\text{hydrazine}}/k_{\text{gl}}$, $k_{\text{HO}_2^-}/k_{\text{CF}_3\text{CH}_2\text{O}^-}$, and $k_{\text{HO}_2^-}/k_{\text{HO}^-}$, often used as criteria of the α effect, are 1.53, 1.02, and 0.61, respec-

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[3] For a tabulation and discussion of the various mechanistic suggestions to account for the α effect, see T. C. Bruice, A. Donzel, R. W. Huffman, and R. A. Butler, *J. Amer. Chem. Soc.*, **89**, 2106 (1967).

[4] L. R. Fedor and T. C. Bruice, *ibid.*, **87**, 4138 (1965).

[5] J. E. Dixon and T. C. Bruice, unpublished work.

[6] T. C. Bruice, A. F. Hegarty, S. M. Felton, A. Donzel, and N. G. Kundu, *J. Amer. Chem. Soc.*, **92**, 1370 (1970).

[7] R. P. Bell, *J. Phys. Chem.*, **55**, 885 (1951).

[8] R. P. Bell and M. B. Jensen, *Proc. Roy. Soc., Ser. A*, **261**, 38 (1961).

[9] M. J. Gregory and T. C. Bruice, *J. Amer. Chem. Soc.*, **89**, 2327 (1967).

[10] See also R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p 155.

[11] J. E. Dixon and T. C. Bruice, *J. Amer. Chem. Soc.*, **93**, 3248 (1971).

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[13] F. G. Bordwell, W. J. Boyle, Jr., J. A. Hautala, and K. C. Yee, *ibid.*, **91**, 4002 (1969); R. A. Marcus, *ibid.*, **91**, 7224 (1969); A. J. Kresge, *ibid.*, **92**, 3210 (1970); F. G. Bordwell, Jr., J. Boyle, Jr., and K. C. Yee, *ibid.*, **92**, 5926 (1970); F. G. Bordwell and W. J. Boyle, Jr., *ibid.*, **93**, 512 (1971).

[14] F. Hibbert, F. A. Long, and E. A. Walters, *ibid.*, **93**, 2829 (1971).

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Table I
Second-Order Rate Constants for Triton Abstraction from *tert*-Butylmalononitrile-*1-t*

Base	pK_a	k_2, sec^{-1} M^{-1}
H_2O[a]	−1.74	5.89×10^{-6}
$ClCH_2CO_2^-$[a]	2.85	3.25×10^{-3}
HCO_2^-[a]	3.75	2.52×10^{-2}
$CH_3CO_2^-$[a]	4.76	2.31×10^{-1}
OH^-[a]	15.75	2.48×10^{5}
Glycinamide	8.10	30.4
Hydrazine	8.16	46.6
2-Methoxyethylamine	9.43	184
Trifluoroethylamine	5.71	1.03
Methoxylamine	4.69	0.176
Trifluoroethanol	12.37	1.49×10^{5}
Hydrogen peroxide	11.6	1.53×10^{5}

[a] F. Hibbert, F. A. Long, and E. A. Walters, *J. Amer. Chem. Soc.*, **93**, 2829 (1971).

tively, which supports the conclusion of a lack of an α effect. In contrast, from the relationship of β and the value of the α effect alluded to previously,[12] the ratio of $k_{\text{hydrazine}}/k_{\text{gl}}$ would be anticipated as *ca.* 40. Of the various rationales which have been put forth to explain the α effect, that of repulsive interaction of adjacent electron pairs[17] appears most useful in explaining the relationship of the α effect to the Brønsted β constant as well as the finding of no α effect for proton abstraction. Thus, the more productlike the transition state the less available are the bonding electrons and the greater is the relief of repulsion. The lack of an α effect for proton abstraction from a carbon acid may be ascribed to the anticipated lessened perturbing influence of a proton upon the electron structure of a base.[18]

Registry No.—Glycinamide, 598-41-4; hydrazine, 302-01-2; 2-methoxyethylamine, 109-85-3; trifluoroethylamine, 753-90-2; methoxylamine, 67-62-9; trifluoroethanol, 75-89-8; hydrogen peroxide, 7722-84-1; *tert*-butyl malononitrile-*1-t*, 33407-05-5.

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Stereochemistry of Iminoxy Radicals Derived from Some Benzohydroximoyl Chlorides

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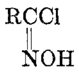
The formation of iminoxy σ radicals by oxidation of oximes in organic solvents using ceric ion[1] or lead tetracetate[2,3] is well established. The electron resonance spectra of these radicals are strongly dependent on their geometrical structure,[2,3] since the transmission of spin density through space by direct overlap or through the framework of the molecule is greatly affected by the relative orientation of the σ orbital containing the unpaired electron and of the interacting nuclei. For instance, in the anti radical from benzaldoxime, a definite coupling constant of 1.4 G with the ortho protons of the aromatic ring is observed, whereas in the syn isomer there is no interaction with any of the phenyl protons;[3] moreover, the splitting due to the hydrogen of the iminoxy group is considerably different in the two configurations, *viz.* 27 G in the syn and 6.5 G in the anti form.[3] Consequently, the marked stereochemical dependence of the hyperfine splitting (hfs) constants of the coupled nuclei in the iminoxy radicals gives a means of obtaining information concerning their molecular geometry.

We wish to report the results of an esr study on iminoxy radicals derived from benzohydroximoyl chlorides (**1–8**). The aim of this investigation was to assign the molecular geometry of these radicals from hfs parameters. The configuration on the C═N bond and the conformation on the N–O bond of hydroximoyl chlorides have been recently investigated through the analysis of dipole moment data.[4] Even though the results were less reliable than in studies of other oximino compounds[5] and imidoyl chlorides,[6] they favor the *E* ap (anti, trans) form. This assignment differs from that given by Lumbroso and coworkers, who preferred the *Z* ap (syn, trans) form.[7]


$$\begin{matrix}\mathrm{RCCl}\\ \|\\ \mathrm{HON}\end{matrix}$$
E ap


$$\begin{matrix}\mathrm{RCCl}\\ \|\\ \mathrm{NOH}\end{matrix}$$
Z ap

The radicals have been generated at room temperature by oxidation of the hydroximoyl chlorides with lead tetracetate in deoxygenated solutions of benzene or methylene chloride. Several compounds were examined, but in some cases the decay of the radical produced was so rapid that the esr spectrum could not be recorded. The compounds giving detectable concentrations of the radical for a sufficiently long time and their hyperfine splitting constants are listed in Table I. In each case the esr spectrum of the observed radical shows the presence of only one of the two geometric isomeric forms either in benzene or methylene chloride. This behavior differs from that of other oximino compounds, such as aldoximes and ketoximes, which usually give a mixture of syn and anti radicals in methylene chloride or other polar solvents.[1–3] The nature of the atom X in the CX═NOH group seems to be very important in determining the stability of the isomeric

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