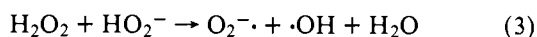
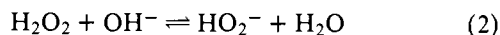
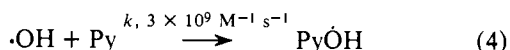


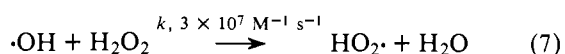
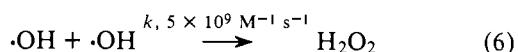
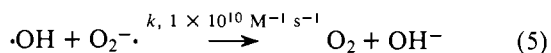
e.g., by decomposition of the perhydrate of potassium peroxide, $K_2O_2 \cdot 2H_2O_2$,⁷ a self-consistent reaction scheme is proposed:



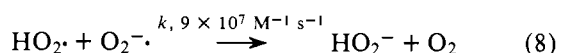
The initial neutralization step is followed by an anion induced disproportionation step. Pulse radiolysis data indicate that the reaction of $\cdot OH$ with pyridine is rapid:⁸



Hence, pyridine should trap and react with $\cdot OH$ ⁹ before it can participate in several well-characterized subsequent reactions:¹⁰

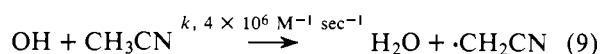


In pyridine the net result of reactions 2, 3, and 4 is the production of 0.5 mol of $O_2^{\cdot-}$ /mol of added base. When the ratio of base to H_2O_2 is low, oxygen can be produced by reaction of a small but finite concentration of HO_2^{\cdot} with $O_2^{\cdot-}$:



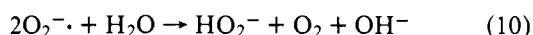
The HO_2^{\cdot} is produced by reaction of $O_2^{\cdot-}$ with H_2O_2 or water.¹¹

The reaction of $\cdot OH$ with acetonitrile is much slower¹² than with pyridine:



Hence, reaction 5 becomes competitive with reaction 9. Consideration of the relative rates that can be calculated for these reactions (assuming that the aqueous rate constants are the same in the acetonitrile solvent) indicates that only some 10–20% of the $O_2^{\cdot-}$ that is formed by reaction 3 would be converted to O_2 . Apparently the radical product (or products) of reaction 9 converts the remaining $O_2^{\cdot-}$ to O_2 to give the observed yield of 0.5 mol of O_2 /mol of H_2O_2 without consumption of OH^- . Reactions 2, 3, and 5 appear to represent a viable mechanism for the base-catalyzed decomposition of H_2O_2 to oxygen and water (as expressed by reaction 1).

The same processes that dominate the base-induced decomposition of H_2O_2 in acetonitrile probably also occur in aqueous solutions of H_2O_2 . However, a second pathway for $O_2^{\cdot-}$ decomposition, in addition to reaction 5, is likely in aqueous solutions (via reaction 8).



In the presence of a large excess of the spin trap, PBN, a substantial fraction of the $\cdot OH$ is trapped (as is the case with pyridine solvent) and O_2 evolution by means of reaction 5 is blocked.



The primary step represented by reaction 3 is presumed to be much faster in pyridine and acetonitrile than in water because of the general enhancement of the nucleophilic reactivity of HO_2^- in aprotic solvents.

The base-induced decomposition of H_2O_2 offers several potentially useful applications. (a) It provides a convenient method to produce $O_2^{\cdot-}$ in pyridine. The only other products

apparently are inert. (b) It also provides a means to generate $\cdot OH$, which, in solvents like CH_3CN and H_2O , has sufficient long lifetimes to react with substrates whose reaction rates are competitive with reaction 5. (c) It may give a means to react $\cdot OH$ and a substrate without interfering side reactions or parallel processes. A possible approach is the use of the substrate as the solvent for the $H_2O_2 + HO_2^-$ reaction.

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- (9) Products of the presumed reaction between $\cdot OH$ and pyridine have not been identified. The mixture of reaction products exhibits no ESR spectrum except that for $O_2^{\cdot-}$. With the exception of O_2 and $O_2^{\cdot-}$, the product solution does not contain species that are electroactive in the range from +1 V to -1 V vs. SCE. Only a very weak absorption (λ_{max} 313 nm) is observed before the pyridine cutoff. The initial step of the reaction is presumed to be addition of $\cdot OH$ to pyridine. Reaction products which have been considered, but whose presence has not been confirmed or excluded, include pyridine *N*-oxide, 2-pyridone (2-hydroxypyridine), bipyridine, and *N*-(2-pyridyl)pyridinium ion.
- (10) The rate constants are from pulse radiolysis studies in aqueous solutions, ref 8; reaction 5, p 39; reaction 6, p 38; reaction 7, p 35.
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Relationship between Charge Delocalization and Stability of Some Oxocarbenium Ions

Sir:

Recently there has been increasing interest in the relationship between the delocalization of charge by substituents on organic ions and the thermodynamic stability of those ions.^{1–3} Two generalizations are frequently made. One is that for a homologous series of compounds or ions extraneous effects will cancel and the ¹³C chemical shift will mirror the changes in charge density on carbon.^{4,5} The other is that the more charge is delocalized, the more stable the ion.³ To date, two exceptions to the above generalizations have been recognized.^{1,2} We wish to draw attention to three additional systems for which the above relationships cannot both be true.

Data for the three additional exceptional systems are given in Tables I and II. It is obvious that these data are inconsistent with at least one of the above generalizations. Consider first the ketones. Comparing the heats of protonation, protonated acetone is the most stable while protonated benzophenone is the

Table I. Relative Ion Stabilities and ^{13}C Chemical Shift of the Carbonyl Carbon in Protonated Ketones and Carboxylic Acids

R	R'	pK ^a	ΔH_{R_1} (kcal/mol) ^b	$\delta^{13}\text{C}$, RCOR' ^c	$\delta^{13}\text{C}$, RC(=OH)R' ^d
			$\begin{array}{c} \text{+O-H} \\ \parallel \\ \text{R-C-R}' \end{array}$		
Me	Me	-7.2	-19.1 ± 0.1	-12.3	-55.7
Me	C ₆ H ₅	-6.2 (-4.32) ^e	-18.9 ± 0.2	-3.2	-25.8
C ₆ H ₅	C ₆ H ₅	-6.2 (-4.97) ^e	-16.9 ± 0.3	-2.4	-15.4
			$\begin{array}{c} \text{+O-H} \\ \parallel \\ \text{R-C-OH} \end{array}$		
Me		-6.10 ^f		15.6 ^g	1.6 ^g
C ₆ H ₅		-7.38 ^f		19.7 ^g	12.0 ^g

^aData from E. M. Arnett, *Prog. Phys. Org. Chem.*, 1, 223 (1963). ^bData from ref 8. ^cJ. B. Stothers and P. C. Lauterbur, *Can. J. Chem.*, 42, 1563 (1964). ^dIn parts per million from $^{13}\text{CS}_2$; data from ref 2b,c. ^eData from ref 6. ^fData from M. A. Paul and F. A. Long, *Chem. Rev.*, 57, 1 (1957). ^gIn parts per million from $^{13}\text{CS}_2$; data from G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, 89, 7072 (1967).

Table II. Relative Ion Stability and ^{13}C Chemical Shifts for the Acyl Carbon in R— $^+\text{C}=\text{O}$

R	ΔH^a (kcal/mol)	$\delta^{13}\text{C}$, ^b RCOCl	$\delta^{13}\text{C}$, R— $^+\text{C}=\text{O}$ ^c
Me	-21.3 ± 0.2	23.8	44.3
C ₆ H ₅	-15.9 ± 0.3	25.0	40.0

^a Heat of transfer from CCl₄ to 11.5 mol % SbF₅ in FSO₃H₂, both at 25 °C, measured calorimetrically as before: J. W. Larsen, P. A. Bouis, M. W. Grant, and C. A. Lane, *J. Am. Chem. Soc.*, 93, 2067 (1971); E. M. Arnett and J. W. Larsen, "Carbonium Ions", Vol. 1, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1968. ^b In parts per million from CS₂; data from ref c (Table I). ^c In parts per million from CS₂; data from reference in g (Table I).

least stable. The $\delta^{13}\text{C}$ (or $\Delta\delta^{13}\text{C}$) indicates that the highest charge density on the carbonyl carbon is to be found in protonated acetone, the most stable ion. The ion with the lowest charge density and presumably the greatest amount of charge delocalization is the least stable. The picture is complicated somewhat if pK values for the ketones are used. These give the same basicity for acetophenone and benzophenone, both being more basic than acetone. The basicity order expected from the ^{13}C measure of charge delocalization (C₆H₅COC₆H₅ > C₆H₅COCH₃ > CH₃COCH₃) is not observed. However, a recent very careful determination shows that acetophenone is slightly more basic than benzophenone.⁶ The difference between these values and the older ones is a good illustration of the experimental difficulties encountered. From Arnett's work,⁷ one expects pK and ΔH to show the same behavior. There are two possible explanations for the discrepancy. One is the notorious difficulty in measuring accurate pK values for simple ketones using acidity function techniques.⁸ The other is large solvation differences resulting in a large variation in the entropy of protonation. We feel the calorimetric data are more reliable. The same trends are seen with protonated carboxylic acids and acylium ions. The acyl cation data led Olah to state "This positive charge is better delocalized in the benzoyl than in either the acetyl or propionyl systems". It makes no difference whether the $\delta^{13}\text{C}$ or $\Delta\delta^{13}\text{C}$ on ion formation is used, the results are still the same.

These data do not indicate which of the generalizations is breaking down. The effect of solvent in these systems may be important and a comparison of gas phase and solution behavior would be most interesting, albeit complicated by the possibility of protonating the aromatic ring in the gas phase.⁹ Discussion of this will be deferred to a full paper now in preparation.

The notion that charge delocalization results in increased stability stands near to the heart of organic chemistry. Likewise, the use of $\delta^{13}\text{C}$ has proved a very powerful tool for investigating charge densities in a variety of molecules, one which

is being used with increasing frequency and circumspection. It is clear that some rather stringent limitations will have to be placed on one of these.

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Nonaqueous Reductive Lanthanide Chemistry. 1. Reaction of Lanthanide Atoms with 1,3-Butadienes¹

Sir:

The known chemistry of the lanthanide elements is rather limited when compared with the chemistry of the transition metals. The variety of ligands found in complexes of the lanthanide metals is small,² and nearly all the chemistry centers on the +3 oxidation state.³ In efforts to demonstrate experimentally a broader chemistry for the lanthanide metals, we have begun an investigation of the nonaqueous reductive chemistry of these elements. Specifically, we wish to determine if lower oxidation states are accessible in insoluble complexes or obtainable transiently in reactions centering on these metals. We anticipate that the lanthanide metals in lower oxidation states will display unusual and perhaps unique chemistry which can be exploited in general synthetic schemes as well as in the synthesis of lanthanide complexes.

The metal atomization technique has been shown to be a useful method for the synthesis of low and zero valent transition metal complexes of low stability^{4,5} and we describe here the use of this technique to make a new class of organolanthanide complexes. Metal atomization has previously been employed preparatively with lanthanide metals to synthesize the trivalent molecules Nd₂³⁺(C₈H₈²⁻)₃,⁶ Ln³⁺(acac⁻)₃,⁷ and