The contribution of each mechanistic pathway to the exchange reaction has now been assessed. The percentage of the exchange reaction proceeding by the proposed pathway through loss of the N-bound proton from O-protonated amide is shown in the eighth row of Table I. In all three cases the new pathway predominates and occurs to an extent greater than 90% for two of the amides. Though it is also predominantly O-protonated, urea undergoes fast nitrogen-bound proton exchange *via* the N-protonated species of the first pathway.[4]

The specific rate constant for loss of N-bound proton from O-protonated amide, k_5, is calculated from k_5/K_a as the K_a is known. The results appear in the ninth row of Table I. The acidity constant $K_{56} = k_5/k_6$ may be approximated by taking $k_6 = 10^{10.3}$ sec^{-1} M^{-1}, the rate constant expected for diffusion-controlled reprotonation in the favored direction.[7] The estimates tabulated as pK_{56} values are listed in the last row of Table I. All of these values lie within the range of those measured for Schiff bases of aliphatic amines.[8]

Amide exchange rates in the presence of metal ions are most easily interpreted by the proposed mechanism. Li^+ decreases and K^+ increases proton exchange of *N*-methylacetamide.[9] We suggest that both metal ions complex weakly at the carbonyl oxygen, accelerating exchange by the new pathway, but at the high concentrations of metal ions employed this effect is offset in the case of Li^+ by a reduction in the activity of water, which is necessary as a proton acceptor in both mechanistic pathways. Amide complexation is stronger for the heavier alkali metal ions and reduction in the activity of water greater for the lighter ones, accounting for the trends in observed exchange rates. That the most basic site on an amide is the carbonyl oxygen is also supported by X-ray studies where coordination at the oxygen occurs even for transition metal ions that might be expected to favor binding at nitrogen more than does a proton.[10] Metal ion coordination at nitrogen occurs after deprotonation of the amide nitrogen when it becomes the most basic site.[11] Even though O-coordination is dominant, small amounts of N-coordinated species may be kinetically significant for the more covalent metal ions as in the Ag^+-catalyzed isomerization of *N*,*N*-dimethylacetamide.[12]

Finally, observation of acid-catalyzed exchange of amide protons in polyacrylamide without isomerization may be accounted for by exclusive occurrence of the proposed pathway.[13] This mechanism also applies to acid and metal ion catalyzed amide hydrogen exchange in peptides and proteins.

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Polar Effects in Radical Reactions. II. A Positive ρ for the Reaction of *tert*-Butyl Radicals with Substituted Toluenes[1]

Sir:

The reactions of free radicals often show substituent effects which resemble those of ionic reactions.[2-6] For example, although it was not anticipated[7-9] that the Hammett equation would be useful for radical reactions, actually a number of radical reactions are correlated excellently by it.[2,3,6,10] The usual explanation[2-6] of this is that the transition states of radical reactions are stabilized by dipolar resonance structures.

The notion that polar resonance structures might stabilize the transition states of certain radical reactions was first suggested in 1945–1947,[2] and it has since been used in a wide variety of contexts.[2-6,10-12] The effect can be depicted as in eq 1, where X· is the radical and

$$\mathrm{X\cdot + QH \xrightarrow{k_a} [\underset{\mathbf{1}}{X\cdot\ \dot{H}\ \cdot Q} \longleftrightarrow \underset{\mathbf{2}}{\dot{X}:^-\ H\ ^+Q} \longleftrightarrow \underset{\mathbf{3}}{X^+\ \dot{H}\ ^-:Q}]} \qquad$$

$$\longrightarrow \mathrm{XH + Q\cdot} \qquad (1)$$

QH is a generalized hydrogen donor or is a substituted toluene if the Hammett equation is to be applied. The use of ionic structures for the transition state[13] of a radical reaction is analogous to their inclusion in the valence bond description of neutral molecules. Pauling, for example, has used such ionic structures to explain the enhanced bond strength which results in X–Y when X and Y differ in electronegativity,[14] and Coulson has rationalized the concept of partial ionic character.[15] In view of this pragmatic utility and solid theoretical foundation, it is not surprising that the use of dipolar structures in rationalizing radical reactions has received wide acceptance.[2-6,16]

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One feature of the Hammett treatment of eq 1 has long drawn notice: all of the ρ values in the literature for hydrogen abstraction from toluenes by free radicals are negative. This has been rationalized[2–6] by the observation that the X· radicals studied to date are electrophilic; for such cases, structure **2** is more important than **3**, and negative ρ's result. We here report the first positive ρ value for eq **1**; we have studied the case where X = *tert*-butyl, and for this radical form **3** appears to be more important than **2**.

Recently, Zavitsas[17–19] has proposed that the order of reactivity of toluenes simply parallels their benzylic C–H bond strengths "without postulating charge separation in the transition state."[18a] A fundamental feature of his treatment is that all radicals must yield negative ρ values. The *tert*-butyl radical is acknowledged to be a key test of this new approach; Zavitsas predicts[18b] a ρ of -1.4 for this radical based on his bond dissociation energy argument. The polar effects concept would postulate that form **3** was more important for *tert*-butyl than for methyl; the *tert*-butyl radical, therefore, should have a more positive ρ than methyl, a radical for which we have reported a ρ of about zero at 100°.[20,21–24]

Figure 1 shows a plot of relative values of k_a (eq 1) for abstraction of hydrogen by *tert*-butyl radicals from toluenes. The *tert*-butyl radicals were generated by photolysis (Rayonet reactor, BL lights) of 2,2′-azoisobutane (AIB) or *tert*-butyl peroxypivalate (BPP) in a mixture of toluene (QH) and deuterated thiol (RSD). Values of k_a relative to k_{SD} for deuterium abstraction from the thiol were determined from the ratio of mass 43 (from *tert*-BuH) to mass 44 (from *tert*-BuD). Two thiols of differing bond strengths give similar results (systems I and III, Figure 1).

A plot of the ratio of mass 43 to 44 *vs.* [QH]/[RSD] should give a straight line with slope equal to k_a/k_{SD}, providing that the usual steady-state assumptions are met and that hydrogen abstraction from the toluene is the only important source of *tert*-BuH. Other possible sources are (1) H abstraction from the R portion of RSD (or from impurity RSH), (2) induced decomposition caused by *tert*-butyl radicals, and (3) cage or (4) free solution disproportionation of *tert*-Bu· radicals. The following considerations show that all these sources can be neglected.

(1) Abstraction of H from RSD or a constant amount of RSH impurity affects the intercept of the plot but not the slope. (2) Induced decomposition does not occur since thermolysis of BPP or azoisobutyronitrile in a solution of AIB in toluene does not produce any change in the concentration of AIB. (3) Disproportionation of *tert*-Bu· in the cage yields negligible[25a] *tert*-BuH since both BPP and AIB give similar results (Figure 1), but BPP does not give a cage yield of *tert*-BuH.[25b] (4) The disproportionation of free *tert*-Bu· radicals in solutions containing thiol would not[26] be expected. Disproportionation can be proved to be negligible by monitoring dimer; dimer yields remain small and constant as the thiol concentration is decreased 30-fold.[27] Isobutane also might be produced by addition of a radical to an aromatic compound to give a cyclohexadienyl radical followed by hydrogen abstraction by a *tert*-butyl radical. This possibility can be eliminated since substituted toluenes are not detected in the product solutions by glpc. In addition, benzene as a QH gives a value of $k_a = 0$.

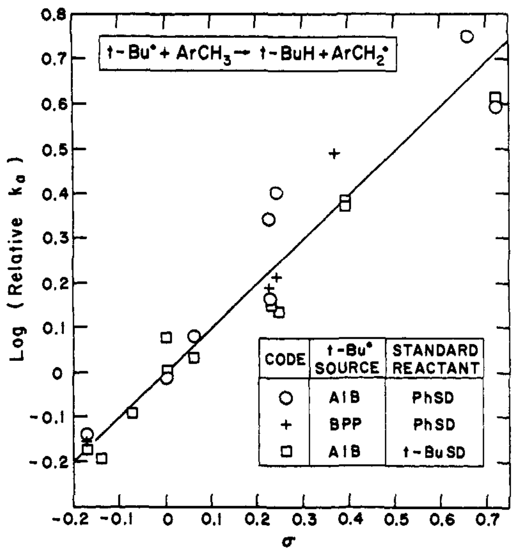

Figure 1. A Hammett equation plot of relative k_a values (eq 1) *vs.* σ constants. For each system, k_n/k_a^0 is plotted, where k_a^0 is the intercept of the least-squares line for that system: system I (○) 0.1 *M* azoisobutane (AIB) and thiophenol-*d*; system II (+) 0.1 *M* *tert*-butyl peroxypivalate (BPP) and thiophenol-*d*; system III (□), 0.1 *M* AIB and *tert*-butyl mercaptan-*d*.

A Hammett σp correlation (see Figure 1) of the data at 30° gives $\rho = 0.99 \pm 0.04$ ($r = 0.96$). This is the first reported positive ρ value for radical abstraction from toluenes.

Finally, we must comment on whether the sign of ρ has any mechanistic significance. A set of similar reactions can be related in one of three ways: they can be isoentropic, isokinetic, or neither.[6,8,9] If they are isoentropic, ρ would always have the same sign and its sign could have mechanistic significance; if isokinetic, ρ may change sign as the temperature is changed, and therefore its sign has little mechanistic significance.

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The data on methyl radicals[20,23] seem to indicate that this radical reacts with toluenes isoentropically, and a review of the data suggests that all atom transfer processes are approximately isoentropic.[28] If this is true, then the ρ value for any given radical reaction always has the same sign but decreases in absolute value as the temperature is raised.[29] Thus, the positive ρ reported here has significance.

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[29] Zavitsas in Figure 1, p 7393, ref 18, uses ρ's at different temperatures; clearly this is unwise.[8]

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A Stable Chromium(IV) Alkoxide of a Secondary Alcohol

Sir:

Extensive evidence of the high oxidative power of chromium(IV) toward organic compounds has been obtained in recent years.[1] In the light of these findings it is not surprising that only a few types of reasonably stable organic chromium(IV) compounds are known: tetraalkoxides,[2] tetrakis(dialkylamides),[3] and tetraalkyls.[4,5]

Until now only tetraalkoxides of tertiary alcohols have been known. Attempts to prepare primary and secondary alkoxides by alcoholysis of tetra-*tert*-butyoxychromium(IV)[2] or tetrakis(dialkylamido)chromium(IV) compounds[3] have been unsuccessful, leading instead to clean oxidation of the alcohol to the corresponding aldehyde or ketone. The mechanism of these oxidations presumably consists of a slow exchange reaction yielding primary or secondary chromium(IV) alkoxides as unstable reaction intermediates which then decompose to chromium(III) species and organic oxidation products.

We now wish to report the preparation of the first stable secondary alkoxychromium(IV) compound, tetrakis(3,3-dimethyl-2-butoxy)chromium(IV). In a typical experiment, 0.5 g of tetra-*tert*-butoxychromium(IV)[6] was added to 6 ml of freshly distilled and degassed pinacolyl alcohol, sealed in an ampoule, and heated in a constant temperature bath at 70° for 36 hr.[7] The contents of the ampoule were transferred to a vacuum line where the alcohols were removed leaving a blue solid; mp 63–64°. *Anal.* Calcd for $C_{24}H_{52}O_4Cr$: Cr, 11.4. Found: Cr, 11.3.

A sample was decomposed with methanol, acidified, and analyzed by nmr; pinacolyl alcohol was the only organic compound (besides methanol) which could be detected. The visible spectrum closely resembles that of the tertiary chromium(IV) alkoxides, with a maximum at 608 nm (ϵ 530) and a shoulder at 730 nm (ϵ 350). The magnetic moment is 3.1 BM.

While tetrakis(3,3-dimethyl-2-butoxy)chromium(IV) is very sensitive to both oxygen and moisture, it is remarkably stable in their absence. A solution of the compound (0.02 *M*) prepared from tetra-*tert*-butoxychromium(IV) and an approximately 150-fold excess of 3,3-dimethyl-2-butanol in dioxane showed less than 1% decomposition over 12 hr at 85°. The pure alkoxide has been stored up to 2 weeks in a sealed flask exposed to normal room light without any apparent decomposition. However, the compound is more sensitive to oxygen and moisture than the *tert*-butoxide. Whereas the latter can be dissolved in methanol giving a blue solution which gradually decays with a measurable rate, the secondary alkoxide reacts almost instantaneously, giving the characteristic reduction product, a gray-green insoluble precipitate which is probably chromium(III) trimethoxide.[8]

The difference in stability of *tert*-butyl methyl carbinolate of chromium(IV) and alkoxides of simple primary and secondary alcohols results from the introduction of bulky *tert*-butyl groups. These groups obviously prevent the molecule from achieving the conformation required for hydrogen transfer in the oxidation step.

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Site Selection of Metal Complexation in the Semibullvalene Skeleton. The Exigencies of Palladation

Sir:

It has been recently discovered that the semibullvalene skeleton possesses a remarkable capacity to react with transition metal complexes.[1] Tungsten hexacarbonyl and silver nitrate form weak complexes which merely perturb the fluxional system, leaving the basic skeleton unchanged.[2] Diiron nonacarbonyl is more drastic in its action and prefers to insert iron into carbon–carbon σ-bonds, the favored site apparently being the weakest

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[1] For recent work on complex formation with molecules containing the vinylcyclopropane grouping see: A. D. Ketley and J. A. Braatz, *J. Organometal. Chem.*, **9**, 5 (1967); T. Shono, T. Yoshimura, Y. Matsumura, and R. Oda, *J. Org. Chem.*, **33**, 876 (1968); A. Eisenstadt, *Tetrahedron Lett.*, 2005 (1972); R. Aumann, *Angew. Chem.*, **83**, 175, 176, 177 (1971); R. M. Moriarty, C.-L. Yeh, and R. Srinivasan, *Tetrahedron Lett.*, 5325 (1972).

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