

Figure 2. (a) Phosphorus atom coordination to rhenium in $\text{ReH}_5(\text{P}(\text{C}_6\text{H}_5)_3)_3$. (b) Proposed coordination geometry for $\text{ReH}_5(\text{MR}_3)_3$ ($\text{M} = \text{P}, \text{As}$). The structure has C_s point group symmetry and may be viewed as a distorted dodecahedron, a distorted truncated octahedron, or a distorted bicapped octahedron.

perature studied, the spectra of both the phosphine and arsine complex show a uniform broadening of all components. This very low-temperature broadening is probably due to increased viscosity of the sample solutions; there is no evidence of further collapse of the intensity two component of the spectra (*i.e.*, of the τ 16.42 absorption) over and above the general broadening. The low-temperature spectra show clearly that three of the five hydride protons in the rigid molecule are magnetically nonequivalent, while the remaining two appear to be equivalent.⁴ Although we consider it unlikely, the possibility remains that the equivalence of two of the hydride protons is not a characteristic of the rigid molecule but results from rapid interchange by a process that is not slowed even at $\sim -155^\circ$.

In order to obtain information about the solid-state geometry of the pentahydride complexes, a partial determination of the crystal structure of $\text{ReH}_5(\text{P}(\text{C}_6\text{H}_5)_3)_3$ ¹ was carried out. A full determination, with usual reliability, was precluded due to the extensive radiation damage suffered by the crystals in Mo $K\alpha$ X-ray beams.

The crystal is monoclinic,⁵ with lattice constants $a = 13.62 \pm 0.02$, $b = 33.14 \pm 0.04$, and $c = 9.92 \pm 0.02$ Å with $\beta = 92.3 \pm 0.1^\circ$. The space group is $P2_1/n$, with four formulas per unit cell and a calculated density of 1.45 g cm^{-3} . Approximate coordinates for the heavy atoms, obtained from solution of the three-dimensional Patterson function, are shown in Table I.

Table I. Approximate Coordinates for the Heavy Atoms in $\text{ReH}_5(\text{P}(\text{C}_6\text{H}_5)_3)_3$

Atom	x	y	z
Re	0.303	0.604	0.199
P(1)	0.167	0.563	0.307
P(2)	0.487	0.612	0.247
P(3)	0.235	0.673	0.151

The corresponding bond lengths are $\text{Re-P}(1) = 2.57$, $\text{Re-P}(2) = 2.55$, and $\text{Re-P}(3) = 2.51$ Å; the interatomic distances are $\text{P}(1)\text{-P}(2) = 4.71$, $\text{P}(1)\text{-P}(3) = 4.08$, and

(4) The presence of two isomers, both of which are fluxional and rapidly interconvert at the highest temperature, is excluded by the observed temperature dependence of the spectra.

(5) $\text{ReH}_5(\text{P}(\text{C}_6\text{H}_5)_3)_3$ may be obtained in three different crystalline modifications (α , β , and γ), all of which give the same molecular species in solution. The α form, studied here, results when the complex is crystallized from CS_2 -petroleum ether (1:4) at 2° : A. P. Ginsberg, to be submitted for publication.

$\text{P}(2)\text{-P}(3) = 4.06$ Å. Bond angles are $\text{P}(1)\text{-Re-P}(2) = 134.3^\circ$, $\text{P}(1)\text{-Re-P}(3) = 107.2^\circ$, and $\text{P}(2)\text{-Re-P}(3) = 107.1^\circ$. Figure 2a illustrates the arrangement of the phosphorus atoms about the rhenium atom; the latter lies 0.49 Å out of the phosphorus atom plane.

Models of the different polyhedra that have been suggested for eight coordination^{6,7} were constructed using the measured bond angles and distances and assuming an Re-H distance of ~ 1.7 Å.⁸ The observed pattern of hydride proton equivalence (1, 1, 1, 2) may be accounted for by geometries based on the dodecahedron, truncated octahedron and bicapped octahedron with caps on adjacent faces. The structures derived from these polyhedra all have C_s point group symmetry and differ from each other only by small hydrogen atom displacements; they are exemplified by Figure 2b.

It does not appear worthwhile, at this stage, to speculate about the mechanism of the fluxional behavior of $\text{ReH}_5(\text{MR}_3)_3$ complexes. However, we note that three distinct mechanisms are required to account for the temperature dependence of the nmr spectra; a number of possibilities are evident from the proposed structure. Further work on these systems is in progress.

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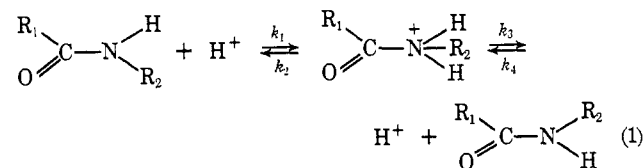
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Predominant N-Bound Hydrogen Exchange via O-Protonated Amide¹

Sir:

The generally accepted mechanism for both acid-catalyzed *cis-trans* isomerization and exchange of nitrogen-bound hydrogens in amides is *via* an N-protonated intermediate (eq 1).² General acid catalysis



has been observed,³ consistent with the first step as rate limiting. Hydronium ion is the only general acid catalyst considered here. Assuming a low steady-state concentration of the N-protonated species, the second-order rate constant for hydrogen exchange of an N-monosubstituted amide is given by $k_N = k_1/2$. Favoring of the *trans* isomer and occurrence of the exchange process in most cases precludes observation of isomerization in monosubstituted amides by proton

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magnetic resonance spectroscopy. Isomerization may be followed in dimethylamides where, by the mechanism above, the second-order rate constant is given by $k_{\text{iso}} = k_1/2$. Thus, by the above mechanism the second-order rate constant for proton exchange in a monomethylamide is given by the same equation as isomerization in the corresponding dimethylamide. Provided the basicities of the two amides are comparable or allowance is made for a basicity difference, the above mechanism predicts that the rate constant for exchange in a monomethylamides will equal that for isomerization in a dimethylamide.

It is known, however, that despite the lower basicity of monomethylamides compared to the corresponding dimethylamides, the observed second-order rate constants for exchange in monomethylamides exceed those for isomerization in dimethylamides. Some results are presented in Table I. The second-order rate con-

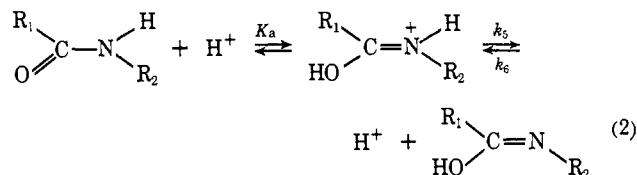
Table I. Hydrogen Exchange and Isomerization of N-Methylated Amides^a

	Benzamide Di- Methyl methyl	Acetamide Di- Methyl methyl	Formamide Di- Methyl methyl			
$k_{\text{ex}}, \text{sec}^{-1} M^{-1}$	490 ^b	400 ^c	12 ^d			
$k_{\text{iso}}, \text{sec}^{-1} M^{-1}$		106 ^b	275 ^e		1.0 ^d	
K_a, M	60 ^f	18 ^f	5.2 ^g	2.4 ^g	33 ^h	22 ^h
$10^{-8}K_{21}, M$	2	0.5	0.4	0.2	70	50
$10^{-6}K_{21}/K_a$	3	3	8	8	200	200
$k_1/2, \text{sec}^{-1} M^{-1}$	32	106	127	275	0.7	1.0
$k_5/K_a, \text{sec}^{-1} M^{-1}$	458		273		11.3	
New path, %	93		68		94	
$10^{-3}k_5, \text{sec}^{-1}$	27		1.4		0.4	
pK_{56}	5.9		7.2		7.7	

^a At or near 25°. ^b This research. ^c Reference 2 and J. E. Bundschuh and N. C. Li, *J. Phys. Chem.*, **72**, 1001 (1968). ^d Estimated from results presented in footnote h. ^e B. G. Cox, *J. Chem. Soc. B*, 1780 (1970). ^f C. R. Smith and K. Yates, *J. Amer. Chem. Soc.*, **93**, 6578 (1971). ^g M. Liler, *J. Chem. Soc. B*, 385 (1969). ^h M. Liler, *J. Chem. Soc. B*, 334 (1971).

stants for the benzamides were determined from the pH of coalescence of the pair of methyl peaks in the pmr spectra obtained in fresh dilute H₂SO₄-H₂O solutions in a Varian HA-100 spectrometer at 26° according to the equation $k = \pi(\text{Hz})/1.41(\text{H}^+)$. For *N*-methylbenzamide the coupling constant $J = 5.1$ Hz for the split methyl peaks which collapse at pH 1.64 ± 0.03 . For *N,N*-dimethylbenzamide the chemical-shift difference is 10.7 Hz between the two methyl peaks which coalesce at pH 0.65 ± 0.03 . Concentrations from 0.1 to 0.3 *M* amide gave the same results. Rate constants for the acetamides were taken directly from the literature while those for the formamides were calculated from published pmr spectra and are the least accurate.

The uniformly greater rates of proton exchange over isomerization in amides may be accounted for by an additional pathway for exchange alone to occur. Following the earlier suggestion,⁴ we propose the following additional pathway for exchange *via* loss of a nitrogen-bound proton from O-protonated amide (eq 2). Isomerization is negligible in the O-protonated species due to increased double bond character in the carbon-



nitrogen bond. The first-order rate constant for exchange by the proposed mechanism is given by $k = k_5[\text{H}^+]/([\text{H}^+] + K_a)$. Doublet collapse in the pmr spectra of the amides occurs in dilute acid solutions where only a fraction of the amide is protonated. Thus, the second-order rate constant by the proposed exchange mechanism becomes $k_0 = k_5/K_a$. Acidity constants, K_a , determined by equilibrium measurements appear in the third row of Table I. The observed second-order rate constant for exchange may then be expressed as the sum of the constants due to the processes occurring in the two mechanisms (eq 3). It is the main

$$k_{\text{ex}} = k_N + k_0 = k_1/2 + k_5/K_a \quad (3)$$

purpose of this communication to assess the contribution of the proposed pathway to the overall exchange rate. Almost incidentally we shall also evaluate the ratio of O- to N-protonated amide species, as the predominance of N-protonated species in dilute acid solutions is still advanced.^{5,6}

For isomerization and the exchange reaction that proceeds by the first mechanism, the reverse reaction is a diffusion-controlled deprotonation in the thermodynamically favored direction so that⁷ $k_2 \approx 10^{10} \text{ sec}^{-1}$. The acidity constant for protonation at the amide nitrogen may then be calculated from $K_{21} = k_2/k_1 = 10^{10}/2k_{\text{iso}}$. These acidity constants are tabulated in the fourth row of Table I. The ratio of O- to N-protonated amide species is given by K_{21}/K_a and these ratios appear in the fifth row of Table I. For all three kinds of amides the ratio of O- to N-protonated species exceeds 10^6 . These results contrast with claims for predominant N-protonation in dilute acid solutions of amides including acetamide⁵ and benzamide.⁶ Coalescence of the two methyl peaks of dimethylbenzamide occurs in weakly acid solutions where, according to its K_a value, less than 2% of the amide is protonated. Because coalescence occurs in weakly acid solutions, studies of isomerization and exchange provide one of the best methods for determination of relative populations of protonated amide species in dilute acids.

To separate the contributions of the two mechanistic pathways to the proton exchange reaction, we evaluate the rate constant for the first pathway from the isomerization rate constant for the dimethylamide. The less basic monomethylamides should possess smaller k_1 values than the corresponding dimethylamides. To estimate $k_1/2$ for each monomethylamide, the rate constant $k_{\text{iso}} = k_1/2$ for the dimethylamide is multiplied by the ratio of K_a values for the di- and monomethylamides. The resulting $k_1/2$ values are tabulated in the sixth row of Table I. For each monomethylamide the value of k_5/K_a may be obtained by subtraction in eq 3; the values appear in the seventh row of Table I.

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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 $k_6 = 10^{10.3} \text{ sec}^{-1} M^{-1}$, 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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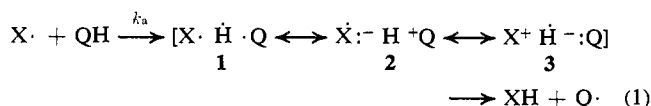
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Polar Effects in Radical Reactions. II. A Positive ρ for the Reaction of *tert*-Butyl Radicals with Substituted Toluenes¹

Sir:

The reactions of free radicals often show substituent effects which resemble those of ionic reactions.²⁻⁶ For example, although it was not anticipated⁷⁻⁹ 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 explanation²⁻⁶ 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 $X\cdot$ is the radical and



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 state¹³ 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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