5-phenylphenanthroline-Fe⁺² complexes at liquid nitrogen temperature; this difference presumably involves a fairly long range effect and suggests that a greater separation between group I and group II complexes might have been expected.

The small difference between group I and group II may perhaps be rationalized in terms of the duality of the bonding of ligands attached to transition metals in low oxidation states. The carbonium ion ligand might be expected to result in a decrease in electron density, including 4s, in iron in the "forward coordination" when compared to a neutral diene and therefore give rise to a positive chemical shift. However, the back donation of d electrons into the carbonium ion ligand would be stronger than for the diene; the resulting lowering of 3d electron density about iron would decrease the shielding of the 4s electron density and thereby cause a negative chemical shift. The two effects would therefore tend to nullify each other. The net result is a small decrease in effective s density and a corresponding positive shift.

The dominance of forward coordination over back donation is also illustrated in the chemical shifts of $Fe(CO)_{5}$ and $Fe(CO)_{3}(PPh_{3})_{2}$ whose stereochemistry differs from the group I and II complexes. The strong electron donating properties of the triphenylphosphine group result in a net negative shift compared to Fe(CO)₅.

In contrast to the small effects of chemical bonding on the shift δ , there exists within each group a considerable variation in splitting Δ . The splitting is observed to be greatest for molecules displaying axial symmetry, such as $Fe(CO)_5$, $Fe(CO)_3(PPh_3)_2$, and 7-acetoxy bi-cycloheptadiene $Fe(CO)_3$. The large effects on the splitting caused by slight structural changes suggests that further analysis of the origins of electric field gradients in these molecules is desirable and may prove helpful in establishing certain stereochemical relations.

Acknowledgment.—We wish to thank Mr. Richard Mazak and Mr. John Travis for some of the experimental measurements and the Alfred P. Sloan Foundation for financial support.

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RECEIVED JUNE 10, 1963	

Effect of Solvents on Transition States in the Reactions of t-Butoxy Radicals¹

Sir:

The major products of reaction of *t*-butoxy radicals in the presence of two potential hydrogen donors are determined by the competition

$$(CH_{s})_{s}C \longrightarrow CH_{s}COCH_{s} + CH_{s}.$$
 (1)

$$(CH_3)_3C - O \cdot + R_1H \xrightarrow{R_{a_1}} (CH_3)_3COH + R_1 \cdot (2)$$

$$(CH_3)_3C \longrightarrow O + R_2H \xrightarrow{\kappa_{32}} (CH_3)_3COH + R_2$$
 (3)

The rate constant k_{a_1}/k_{a_2} may be measured directly from the relative rates of disappearance of R₁H and R₂H or indirectly by determining k_{a_1}/k_d and k_{a_2}/k_d from t-butyl alcohol/acetone ratios obtained in separate experiments in the presence or R_1H and R_2H alone. We wish to report a study of the effect of solvents on these competitions indicating much more significant phenomena than the small solvent effects which have been noted previously in t-butoxy radical reactions.²⁻⁴

(1) Support of this work by grants from the National Science Foundation is gratefully acknowledged.

TABLE I

DETERMINATION OF k_a/k_d IN REACTION OF *t*-BUTOXY RADICALS WITH CYCLOHEXANE

					log
		-ka/kd			$(PZ)_{a}/$
Solvent	100°	40°	0°	$E_{\rm d} - E_{\rm a}$	$(PZ)_{d}$
Gas phase	$(203)^{b}$	$(625)^{b}$	(1040) ^b	10.80	-4.77
C2C13F3	4,29	52.8	487	9.65	-5.04
CH₃CN	$(0.68)^c$	8.12	81.9	9.54	-5.73
C_6H_6	2.82	24.7	207	8.66	-4.63
C6H5CN	1.90	16.9	109	8.28	-4.58
C ₆ H ₅ Cl	2.65	16.4	91.7	7.21	-3.82
C2C14	4.14	39.0	293	8.72	-4.49
C2H2Cl2 (trans)	2.26	14.2	98.9	7.69	-4.16
$C_2H_2Cl_2$ (cis)	1.57	9.12	52.2	7.04	-3.92
СН₄СООН	$(0.65)^{c}$	2.84	12.4	5.80	-3.64
^a Difference i	n activation	energies	kcal /n	iole 👌	At 60 40

At **6**0, 40, and 30° respectively. ^c Extrapolated values.

Our technique involves t-butyl hypochlorite chlorinations in which reactions 1-3 are steps in a chain sequence, followed by reaction of the radicals produced with tbutyl hypochlorite to yield CH₃Cl, R₁Cl, and R₂Cl, respectively, and regenerate $(CH_3)_3C-O^{-3}$ The hypochlorite was decomposed photochemically in excess (5:1)cyclohexane of varying concentrations (0.01-0.5 M) in each of several solvents at 0, 25, 40, 70, and 100° and t-butyl alcohol/acetone ratios determined by gas chromatography. Ratios of k_a/k_d then were obtained from plots of alcohol/acetone ratios vs. cyclohexane concentration. Plots of log k_a/k_d vs. 1/T gave excellent straight lines, and some of our ratios, activation energy differences, and ratios of PZ factors are listed in Table I, which also includes gas phase measurements obtained by a slight modification of the same technique.

We see that k_a/k_d ratios vary by over a factor of 100 at the lower temperatures, chiefly as a consequence of changes in the difference in activation energy for the hydrogen abstraction and β -scission processes. As we have pointed out elsewhere⁵ solvent effects on competitive radical reactions must reflect different degrees of solvent interaction with the transition states rather than with the radicals involved (assuming any such "complexing" to be a rapid process) and solvation of the transition state for a β -scission (or other unimolecular radical reaction) is sterically more feasible than solvation of the transition state for hydrogen abstraction. Our results are consistent with this view. Aromatic solvents and the chloroethylenes⁶ apparently stabilize the transition state for β -scission by 3–4 kcal. over that for attack on cyclohexane, presumably through the contribution of charge-transfer type structures.

$$CH_{3} \xrightarrow[CH_{3}]{CH_{3}} CH_{3} \xrightarrow[CH_{3}]{CH$$

There evidently is no major effect of simple solvent polarity, since energetics in acetonitrile are similar to those in a haloalkane, but the very large facilitation of β -scission in acetic acid suggests that hydrogen bonding is an alternative means of transition state stabilization.

$$\begin{array}{c} CH_3 & O\\ CH_3 \cdots C \cdots O \cdots H\\ CH_3 & O \end{array} C - CH_3$$

⁽²⁾ G. A. Russell, J. Org. Chem., 24, 300 (1959).

⁽³⁾ C. Walling and B. B. Jacknow, J. Am. Chem. Soc., 82, 6108 (1960).
(4) E. L. Patmore and R. J. Gritter, J. Org. Chem., 27, 4196 (1962).

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 ⁽⁶⁾ The chloroethylenes were chosen since they show no significant reaction with t-butoxy radicals. We previously have reported a large effect of olefinic solvents on the reactions of the 2-benzyl-2-propyloxy radical.

⁽⁷⁾ Evidence for hydrogen bonding of peroxy radicals has been given by F. F. Rust and E. A. Youngman, J. Org. Chem., 27, 3778 (1962).

Sir



Fig. 1.—Schematic energy diagram (in kcal./mole) for reaction of gas phase and solvated *t*-butoxy radicals (dashed lines are energy levels of solvated species).

We obtain evidence on the magnitude of solvent participation in the transition state for hydrogen abstraction processes by reinvestigating³ the tertiary/primary chloride ratio obtained in the *t*-butyl hypochlorite chlorination of 2,3-dimethylbutane, Table II. Results are striking in that chlorobenzene and acetic acid *reduce* the measured selectivity, apparently through a decrease in the *PZ* factor for *t*-H abstraction, even though the activation energy difference increases. Evidently solvent participation is important and would increase the selectivity of the *t*-butoxy radical were it not for a large entropy loss associated with a highly restricted orientation for attack of a solvated *t*-butoxy radical on a tertiary hydrogen.

TABLE II

t-BUTYL HYPOCHLORITE CHLORINATION OF 2,3-DIMETHYLBUTANE

		1/p ratio ^a		log	
Solvent	40°	0°	$E_{\rm p} - E_{\rm t}^b$	$(PZ)_{\rm t}/(PZ)_{\rm p}$	
C ₆ H ₆ ^c	55.3	88.6	1990	0.36	
None	44.4	68.5	1850	. 36	
C ₆ H ₅ Cl	38.4	95.4	3420	-0.79	
CH₃COOH	19.5	52.9	4230	-1.66	

^a Relative reactivities (per H) of tertiary and primary hydrogen. ^b Activation energy difference, cal./mole. ^c Data from ref. 3.

The gas phase energetics for β -scission of the *t*-butoxy radical have been estimated⁸ as $E_a = 13$ kcal., $\Delta H =$ 4.7 kcal. Assuming 3 kcal. stabilization of the transition state for hydrogen abstraction in solvents such as acetic acid (which seems a minimum value in view of the changes in $E_p - E_t$ in Table II) we can construct the energy diagram for *t*-butoxy radical reactions shown in Fig. 1. This indicates a stabilization of the transition state for β -scission of 7–8 kcal., a plausible value for strong hydrogen bonding, and we have used the same value for the ground state radical.

More extensive data and discussion on these systems will be published elsewhere, but it is evident that solvent effects in *t*-butoxy radical reactions are much more pronounced than had been realized previously.

(8) P. Gray and A. Williams, Chem. Rev., 59, 239 (1959)

(9) National Science Foundation Predoctoral Fellow, 1961-1963.

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Received June 5, 1963

Configuration of the Porphine Skeleton in Unconstrained Porphyrin Molecules^{1,2}

The classical X-ray diffraction analyses of crystalline structure for the phthalocyanines³ are generally cited in support of a naturally planar configuration for the porphine skeleton in porphyrins, whereas two recent analyses of nickel etioporphyrin-I⁴ and copper tetraphenylporphine⁵ assign nonplanar configurations to the porphine skeleton in the crystalline materials. Application of relevant theory to the accurate stereochemical data presented below for tetraphenylporphine provides a mutual accommodation of the earlier observations, and other general conclusions of interest.

Apart from obvious differences at the molecular center, tetraphenylporphine is isostructural with the copper derivative,⁵ and we employ an analogous notation for the asymmetric grouping in the tetragonal space group 142d. The four-molecule cell has $a = 15.125 \pm 0.025$, $c = 13.94 \pm 0.02$ Å. The required molecular symmetry (vide infra) is S₄ - 4. The 892 observed {hkl} intensities correspond to a 91% yield with Cu Ka radiation. Least squares refinement which utilized anisotropic thermal parameters, followed by difference synthesis, furnish the stereochemical data of Fig. 1. Standard deviations for bond parameters



Fig. 1.—Diagram in true projection along the $\overline{4}$ axis (c of the crystal) of a portion of the tetraphenylporphine skeleton (and of the appropriate metal derivative). The skeletal ruffling is to negative z in the first and third quadrants, to positive z in the second and fourth.

within the porphine skeleton are 0.006-0.008 Å. for lengths, *ca*. 0.4° for angles; mostly larger and more variable values apply to the phenyl group. With two less satisfactory peripheral exceptions, quantitatively plausible positions for hydrogen atoms, including the "half-atoms" attached to nitrogen, are directly indicated by the difference maps.

Maximum deviations from planarity within the porphine skeleton occur at methine carbon; the z-coordinate alternates between -0.38 and +0.38 Å. for each rotation of 90° about c. Besides the pyrrole and benzene rings, the following key groupings are flat within experimental accuracy: $C_6C_5C_8C_{10}$, $C_1^{a}C_5N^{a}C_2^{a}$, $C_4C_5NC_3$, $C_5C_6C_1^{a}C_4$. The angle between the planes of

(I) Supported by the U. S. Public Health Service, the National Science Foundation, and the Advanced Research Projects Agency. We thank also the Cornell Computing Center, R. C. Lesser, Director.

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⁽²⁾ Our very pure tetraphenylporphine was prepared by A. A. Adler and W. Shergalis, with support from the U. S. Signal Corps (Grant DASIG-36-039-61-G9). An account of their work will appear soon.