photooxidation. We are currently exploring this possibility by use of cation-exchange techniques.

Photooxidation of Ru(II) necessitates the corresponding reduction of some solution species. Sigwart and Spence[1] suggest the reduction of coordinated N_2 in the photolysis of Ru(II)–N_2 complexes since mass spectrometer experiments did not reveal H_2 as a reaction product. However, in photolysis of argon-deaerated $Ru(NH_3)_6{}^{2+}$ and $Ru(NH_3)_5H_2O^{2+}$ solutions, H_3O^+ or H_2O appears to be the most likely oxidant. We have demonstrated in nonquantitative mass spectrometer experiments that the full-beam photolysis of $Ru(NH_3)_5$-py^{2+} ($\sim 4 \times 10^{-3}$ M, BF_4^- salt) does produce H_2 in easily detectible quantities. Whether the formation of H_2 is a minor or major pathway in the photolysis of this ion and of the other Ru(II) ammines shall be elucidated by more quantitative experiments which are being initiated. Despite the care taken in deaerating the solution, we have not excluded the possibility of trace quantities of O_2 also acting as the electron acceptor. Nevertheless, the reproducibility of the photooxidation yields and the stability in the dark of $Ru(NH_3)_5H_2O^{2+}$ solutions (which are sensitive to O_2) argue against this suggestion.

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Difluorophosphoryl-μ-oxo-difluorophosphine. A Novel Mixed Valence Phosphorus Oxyfluoride

Sir:

The recent mention of compounds containing phosphorus in two valence states[1] prompts us to report our work on the preparation of $F_2POP(O)F_2$. We have prepared the compound in 40% yield by the photolysis of $P(O)F_2Br$ in the presence of mercury at 23°.
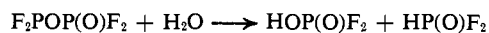
$$2P(O)F_2Br + excess\ Hg \xrightarrow{2537\ Å} F_2POP(O)F_2 + Hg_2Br_2$$
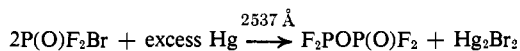
Other products formed include POF_3, F_2POPF_2, $P_2O_3F_4$, PF_3, and unidentified colored solids. Purification of $F_2POP(O)F_2$ was accomplished by fractionation through traps of -78 and $-195°$. The product and a small amount of $P_2O_3F_4$ were retained in the $-78°$ trap.

Difluorophosphoryl-μ-oxo-difluorophosphine is a colorless liquid [mp $-31°$, bp 48°, vapor density molecular weight 174 (calcd for $P_2O_2F_4$, 170.0)] which decomposes slowly at 23°. The ^{19}F nmr, infrared, and chemical reactivity are all consistent with the presence

(1) R. G. Cavell, T. L. Charlton, and A. A. Pinkerton, *Chem. Commun.*, 434 (1969).

of both trivalent and pentavalent phosphorus atoms. The ^{19}F nmr spectrum obtained in 25% $CFCl_3$ at 34.5° showed two doublets of equal area centered at φ 38.3 (F_2PO) and 81.2 ($OP(O)F_2$) with $J_{PF} = 1412$ and 1033 Hz, respectively.[2,3] The resonance attributed to OP-$(O)F_2$ was slightly broadened at 34.5°. On cooling to $-26°$ (at lower temperatures the sample froze), a symmetrical complex multiplet of the type A_2B_2XX' was formed. The F_2PO resonance, however, remained sharp at this temperature. The infrared spectrum of $F_2POP(O)F_2$ contained absorptions at (cm^{-1}): 1385 (s), P=O; 1024 (vs), P–O–P; 975 (s), P–F; 910 (w); 868 (s), P–F; 721 (m); 510 (m); 445 (w). The assignments are based on comparison with $F_2POPF_2{}^4$ and $F_2P(O)OP(O)F_2$.[5] Further proof of the unsymmetrical structure of $F_2POP(O)F_2$ was obtained by reaction with HCl. Stoichiometric amounts reacted nearly quantitatively at 23° forming $HOP(O)F_2$ and PF_2Cl.

The decomposition of $F_2POP(O)F_2$ appeared to be catalyzed by impurities, and considerable decomposition was often observed in the vacuum system. However, a 2-mmole sample was kept for 2 weeks in a sealed 100-ml Pyrex bulb without complete decomposition. The compound was extremely sensitive to traces of water and some $HOP(O)F_2$ was almost always observed along with PF_3 and F_2POPF_2. The effect of impurities and exact stoichiometry are not yet known, but our results to date are consistent with the following equations and previously reported instability of $F_2POPF_2{}^4$ and HP-$(O)F_2$.[6,7]

$$2F_2POP(O)F_2 \longrightarrow F_2POPF_2 + F_2P(O)OP(O)F_2$$

$$F_2POP(O)F_2 + H_2O \longrightarrow HOP(O)F_2 + HP(O)F_2$$

$$HP(O)F_2 + F_2POP(O)F_2 \longrightarrow F_2POPF_2 + HOP(O)F_2$$

$$F_2POPF_2 \longrightarrow PF_3 + (POF)_n$$

Further studies of the decomposition and other chemical reactions of $F_2POP(O)F_2$ are in progress along with a detailed analysis of the temperature-dependent nmr.

Acknowledgment. The author thanks D. T. Dix and R. G. Czerepinski of the Dow Chemical Co. for the nmr spectra. The partial support of this work by the National Science Foundation is gratefully acknowledged.

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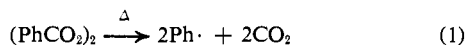*Received August 22, 1969*

A Molecular Orbital Correlation of the Rates of Formation of Arylmethyl Radicals

Sir:

In the past decade attempts to correlate the rates of formation of arylmethyl carbonium ions and carban-

ions with MO calculations have met with success.[1,2] However, a corresponding effort to correlate similar radical systems had failed.[3] We wish to report successful correlations of the rates of hydrogen abstractions from a series of unsubstituted arylmethanes by the trichloromethyl radical, generated from bromotrichloromethane at 70.0 ± 0.1°, with the differences in π-binding energy, ΔE_π, between the intermediate radical and the arylmethane reactant. ΔE_π was determined both by the simple HMO approach and by an SCF–LCAO–MO open-shell calculation.[4]

The hydrogen-abstraction reactions were run in replicate relative to 1-methylnaphthalene. Reactions were carried out in sealed ampoules, under a nitrogen atmosphere, with benzene–bromotrichloromethane as the solvent and benzoyl peroxide as the radical initiator. The samples were analyzed by glpc using o-dichlorobenzene as the internal standard. Solutions of the two arylmethanes, benzoyl peroxide, o-dichlorobenzene, bromotrichloromethane, and benzene, were prepared in the approximate ratio 0.5:0.5:0.1:1:10:15. Small portions of the solutions were reserved for analysis of starting material. The remainders were then divided among the ampoules. The reaction sequence is shown in eq 1–4.

$$(PhCO_2)_2 \xrightarrow{\Delta} 2Ph\cdot + 2CO_2 \qquad (1)$$

$$Ph\cdot + BrCCl_3 \longrightarrow PhBr + \cdot CCl_3 \qquad (2)$$

$$ArCH_3 + \cdot CCl_3 \xrightarrow{rds} ArCH_2\cdot + HCCl_3 \qquad (3)$$

$$ArCH_2\cdot + BrCCl_3 \longrightarrow ArCH_2Br + \cdot CCl_3 \qquad (4)$$

Ring substitution in arenes by trichloromethyl radical is a well-known reaction occurring under analogous conditions.[5] It can be assumed that this reaction might also take place in the arylmethanes. This competing reaction was taken into account by running the arylmethane in competition with the parent arene. Assuming no large perturbation by the methyl group, the relative rates of methyl hydrogen abstraction to ring substitution can be obtained. In general methyl hydrogen abstraction accounted for between 60 and 100% of the total reaction of the arylmethane. These results are shown in Table I and can be used to convert relative rates of disappearance into relative rates of methyl hydrogen abstraction.

Huyser has shown that the rate-determining hydrogen-abstraction step by trichloromethyl radical is endothermic.[6] Hence, by the Hammond postulate the transition state should resemble the radical intermediate.[7] The relative rates of hydrogen abstraction from the arylmethanes should, therefore, correlate with the differences in π-binding energies between the intermediate radicals and the arylmethane reactants. ΔE_π

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Table I. Relative Rates of Hydrogen Abstractions from a Series of Unsubstituted Arylmethanes by Trichloromethyl Radical at 70°

Arylmethane	% H abstr	$k_x/k_{1\text{-menaph}}$	$-[\Delta E_\pi(x) - \Delta E_\pi(Tol)]^a$ HMO	SCF
Toluene	100	0.172 ± 0.008	(0.00)	(0.00)
1-Methyltriphenylene	84.6	0.362 ± 0.027	0.062	0.076[b]
2-Methyltriphenylene	69.1	0.395 ± 0.014	0.024	0.068[b]
3-Methylphenanthrene	86.9	0.547 ± 0.027	0.033	0.060
1-Methylphenanthrene	69.5	0.569 ± 0.035	0.082	0.139
2-Methylnaphthalene	68.4	0.682 ± 0.057	0.023	0.076
9-Methylphenanthrene	91.0	0.931 ± 0.056	0.092	0.178
1-Methylnaphthalene	94.3	(1.00)	0.091	0.175
6-Methylchrysene	77.0	2.19 ± 0.04	0.117	0.214
2-Methylanthracene	74.5	5.89 ± 0.47	0.048	0.215
1-Methylanthracene	54.3	13.1 ± 1.4	0.113	0.340
1-Methylpyrene	76.5	18.7 ± 1.0	0.147	0.352
9-Methylanthracene	86.4	112.0 ± 5	0.206	0.519

[a] Units are in electron volts. [b] "Long bonds" set equal to 1.48 Å.

was determined by the HMO and SCF–LCAO–MO methods. In the latter, the π-binding energies of the radicals were obtained using a constant resonance integral based on a carbon–carbon bond length equal to 1.40 Å. The suggestion of Pople and Nesbit in maintaining different orbitals for electrons of opposing spin in systems which do not have a closed-shell configuration was followed.[8] Self-consistency in these cases was normally reached after ten iterations. The π-binding energies of the arylmethanes were essentially those of the parent arenes with the methyl groups causing a small inductive perturbation by modifying the ionization potential of the carbon atoms to which they are attached.[9] Results of the kinetic studies and calculations are shown in Table I. The relative rates of abstraction show a spread of three powers of ten and are quite dependent on the position of the methyl group. This is best noted by examining the three methylanthracenes which react over a range of 20.

The log of $k_x/k_{1\text{-menaph}}$ was then plotted against $\Delta E_\pi(rel)$. The coefficients of the correlations (CC) are shown in Table II. From the coefficient of 0.855

Table II. Relative Rates of Hydrogen Abstraction Correlated with $\Delta E_\pi(rel)$

Type of correlation	CC (HMO)	CC (SCF)
All points	0.855	0.977
α-Methylnaphthyl-type points	0.948	0.993
β-Methylnaphthyl-type points	0.904	0.991

obtained from the Hückel treatment of all points, it is obvious that the correlation is not good. The correlation is improved when the data are separated into α-methylnaphthyl-type compounds and β-methylnaphthyl-type compounds, but it is still rather poor. Such dual correlations have been found for the analogous ionic reactions using Hückel calculations. They have been attributed to nonbonded interactions between peri-hydrogens and the exocyclic methylene group in

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the α-methylnaphthyl-type intermediate.[1,2] This is not found in corresponding SCF calculations. Dewar and Thompson have found a single correlation for the relative rates of carbonium ion and carbanion formation.[10]

Further, Gleicher has shown by strain energy calculations that the nonbonded interactions are not as severe as predicted by the Hückel approach.[11] The failure of the Hückel calculation here is probably due to its neglect of the nonuniform electronic field in these ions.[12]

Our results for the SCF correlation of the rates of hydrogen abstraction show an excellent single correlation as is seen in Table II. The correlation coefficient of 0.977 for all points is, to our knowledge, better than any obtained in similar studies. It appears that even in uncharged odd-alternant systems, the SCF approach can yield more precise correlations than can be obtained from the Hückel treatment. This is probably due to the fact that the unpaired electron will interact differently with other electrons depending on whether

they are of the same or opposite spin.[13] This consideration is ignored in the HMO approach.

There is again improvement with a dual correlation. This may reflect a transition state of slightly higher energy for the α-methylnaphthyl-type compounds because of nonbonded interactions. The change, however, is small, and it is difficult to determine whether this small improvement is real or an artifact of the calculations.

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Book Reviews

Introduction to Mass Spectrometry. Instrumentation and Techniques. By JOHN ROBOZ, Air Reduction Co., Inc., Murray Hill, N. J. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1968. xvii + 539 pp. 16 × 23 cm. $20.00.

The Preface to this book states that it has three objectives: to present an introduction to the theory, design, and operation of the various types of mass spectrometers; to provide assistance in the selection of commercial mass spectrometer systems and components by discussing required instrument performance in many fields of applications; to acquaint the reader with the general experimental techniques employed in mass spectrometry and illustrate these methods in typical applications. It does not succeed in these objectives for several reasons.

The book begins with a good Introduction which defines the various terms used in mass spectrometry and gives a brief account of the scope of applications of mass spectrometry. This is followed by a chapter on mass analysis which covers electrostatic and magnetic analysis fairly fully as well as the principles of focusing the ion beam.

The remainder of the book is not up to the standard of these first two chapters and deals with the following subjects. Pages 65-276 are concerned with the remaining aspects of instrumentation and deal with types of mass spectrometers, ion sources, ion detectors, vacuum techniques, sample introduction, and commercial instruments. Part II of the book covers in a further 225 pages the subject of applied mass spectrometry and discusses types of ions in mass spectra, analytical techniques in organic and inorganic chemistry, mass spectrometry in physical chemistry, and miscellaneous applications.

All these chapters are difficult to read because coverage is uneven and aspects of the same topic are dealt with in several places and the cross references are to sections rather than pages so that they are not easily found. For example, in the section entitled "Isotope Ions" which is only three pages long, there are cross references to an appendix, a table, and six other sections.

Much of the material presented consists of trivial information which is often contradicted in other sections (see, for example, the chapter on Vacuum Techniques where elastomeric seals are discussed several times). Again, the chapter on commercial instruments is not at all critical and the mass of trivial facts presented make it very difficult to pick out the real differences in performance and application. Much of the detail cataloged for one specific instrument equally well applies to several other instruments. And many of the figures quoted for performance are lower than those guaranteed by the manufacturers. But, more seriously, many of the statements made are wrong. For example, a cycloidal analyzer is said to give first-order double focusing.

The book is filled with generalized half-truths, and this, coupled with the large number of completely erroneous statements, makes it a book which cannot be recommended. The errors are particularly frequent in the sections which deal with chemical applications where terms such as ion, molecule, atom, and group are used loosely and almost interchangeably. As an example of the statements made, the section on "Re-arrangement Ions" contains in its first paragraph the remarkable statement about the origin of the peak at m/e 29 in the mass spectrum of isobutane that "its appearance can only be explained by assuming isomerization followed by dissociation,

$$i\text{-}C_4H_{10} \longrightarrow n\text{-}C_4H_{10} \longrightarrow C_2H_5{}^+ + C_2H_5 + e^-.\text{"}$$

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Applications de la Dispersion Rotatoire Optique et du Dichroisme Circulaire Optique en Chimie Organique. By PIERRE CRABBÉ, Directeur des Recherches, Syntex S. A., Professeur à l'Université Ibéroaméricaine et à l'Université Nationale Autonome de Mexico. Gauthier-Villars, Paris, France. 1968. 611 pp. 16 × 24.5 cm. 128 F.

This book represents the second edition of a work first published in English, under the title "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry" (Holden-Day, San Francisco) in 1965 (see review in *J. Amer. Chem. Soc.*, 88, 1340 (1966)). As Professor Djerassi says in his Introduction the development of these two techniques in the past 4 years has been most striking and