type basis sets. A detailed report on the crystallographic and molecular orbital studies is in preparation.

Acknowledgment. The author gratefully acknowledges the help of Professor G. A. Olah and M. Comisarow in preparing the crystals and Professor W. N. Lipscomb for some helpful discussions.

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Nucleophilic Substitution at the Alkoxyl Carbon of Imidates[1]

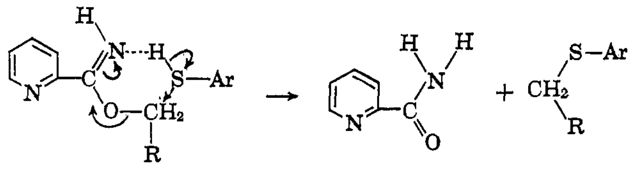
Sir:

It is well known that, generally speaking, substitution in derivatives of carboxylic acids, such as esters and imidates, tends to occur at the central sp^2 carbon rather than at the sp^3 carbon of the alkoxyl group. Exceptions to this trend are the thermal decomposition of imidate hydrochlorides (Pinner cleavage),[2] the alkyl-oxygen fission of esters of tertiary alcohols,[3] and the nucleophilic substitution reactions of esters in which a highly electron-withdrawing substituent (*i.e.*, N-phthalimido)[4] is present at the α-carbon of the alkoxyl group.

In search of a selective method for the replacement of a hydroxyl in polyfunctional alcohols by a suitable nucleophile, the polyfunctional alcohol was first converted to the monoimidate by reaction with 2-cyanopyridine under base-catalyzed conditions,[5] and the resulting imidate was then treated at *ca.* 150° with arylthiols to give the products of the desired nucleophilic substitution reaction at the sp^3 carbon of the alkoxyl group, namely, hydroxyalkyl aryl sulfides, and the novel "leaving group," namely, 2-pyridinecarboxamide.

Thus, the monoimidate of ethylene glycol, upon treatment with *o*- or *p*-thiocresol, *p*-*t*-butylthiophenol, and *p*-bromothiophenol, gave the corresponding 2-hydroxyethyl aryl sulfides in yields as high as 64% of theoretical. The products gave the correct microanalytical results and infrared spectra identical with those of authentic samples prepared by the reaction of the thiols with ethylene chlorohydrin.[6]

The reaction can be carried out in excess of the thiol, or by using diethylbenzene or dimethylformamide as solvent. The yields of the reaction improved when nonpolar solvents were employed, and this observation, as well as the failure of the desired nucleophilic substitution when the hydrochloride or picrate of the imidate was treated with sodium thiocyanate, potassium iodide, or sodium mercaptides, suggest that the reaction occurs in the complex of the imidate and the conjugated acid of the nucleophile by an intramolecular mechanism.


Ar = *o*- or *p*-$CH_3C_6H_4$, *p*-*t*-BuC_6H_4, *p*-BrC_6H_4; R = $HOCH_2$

In accord with the postulated mechanism is the observation that the reactions of benzylamine, piperidine, and morpholine with the imidate derived from 2-cyanopyridine and ethylene glycol produce the conventional attack at the sp^2 carbon. This course of the substitution reaction was proven by the isolation of the N-benzylamide and the N-piperidino- or N-morpholinoamidines (the latter in the form of the picrates), respectively, derived from 2-pyridinecarboxylic acid. Also, the recent report[7] of the formation of thiono esters by the base-catalyzed reaction of imidates with hydrogen sulfide indicates that strong bases, or anionic nucleophiles, react preferentially at the sp^2 carbon, while nucleophiles capable of hydrogen bonding with the imidate favor the intramolecular reaction path leading to the S$_N$ reaction at the sp^3 carbon of the alkoxyl group.

The novel substitution reaction is being extended to more complex polyfunctional alcohols and to nucleophiles other than thiols. Also, the optimum conditions for the reaction are being determined.

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Physical Theory of Chemiluminescence in Systems Evolving Molecular Oxygen[1]

Sir:

Chemiluminescence of organic molecules is a frequently observed phenomenon in liquid reaction systems and most often accompanies oxidation in the presence of hydrogen peroxide or molecular oxygen. An inorganic chemiluminescent reaction system which has been extensively investigated recently[2,3] involves the reaction in alkaline solution of H_2O_2 with either Cl_2 gas or OCl^- (hypochlorite ion). It is now generally agreed that the observed red (and infrared) chemiluminescence in this inorganic case arises from metastable excited states of molecular oxygen produced in the reaction. These observations and interpretations extend the much earlier ones made by Groh and Kirrmann.[4] New observations made in this laboratory now permit the projection of a general theory of chemiluminescence which unites these two classes of phenomena, *i.e.*, organic molecule chemiluminescence in oxidation reactions in solution and excitation of metastable states of molecular oxygen in peroxide systems.

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[1] Work supported in part by a contract between the Division of Biology and Medicine, U. S. Atomic Energy Commission, and the Florida State University, and in part by a contract between the Physics Branch, Office of Naval Research, and the Florida State University.

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In the reaction of H_2O_2 with Cl_2 or OCl^-, luminescence bands have been observed (*cf.* Figure 1) at 12,700 ($^1\Delta_g \rightarrow {}^3\Sigma_g^-$), 7620 ($^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-$), and 6335 A ($2[^1\Delta_g] \rightarrow {}^3\Sigma_g^- + {}^3\Sigma_g^-$). The wavelengths correspond to 0,0 transitions; additional bands corresponding to 0,1 and to 0,2 and in some cases 1,0 vibrational transitions are also observed. The "double-molecule" single quantum transition from the $2[^1\Delta_g]$ state arising from the interaction of two excited oxygen molecules had been known previously only in *absorption* spectra in liquid oxygen,[5] solid oxygen,[6] and high-pressure gaseous oxygen.[7] Higher energy bands corresponding to excitation of molecular pairs to $[^1\Delta_g + {}^1\Sigma_g^+]$ and $2[^1\Sigma_g^+]$ states had also been observed in absorption.[5-7] We have now recorded chemiluminescence at 4780 A corresponding to emission from the $[^1\Delta_g + {}^1\Sigma_g^+]$ double molecule state. The reaction involved Cl_2 gas bubbled through a fritted filter into alkaline 10% H_2O_2 solution, with the same spectrographic equipment used previously[2] but using an ultrafast Polaroid film (Type 410; ASA 10000).

Previous interpretations of organic molecule chemiluminescence have sought chemical mechanisms for excited-state production, especially because the energetics of peroxide breakdown or single molecule oxygen excitation made energy transfer from these species infeasible. However, the emission observed at 4780 A, oxygen chemiluminescence, corresponding to an energy of 59.8 kcal/mole (20,920 cm^{-1}), now offers the possibility of energy transfer to excite, *e.g.*, eosin fluorescence or zinc tetraphenylporphine fluorescence (*cf.* Figure 1); with 1 quantum of vibrational excitation, 63.8 kcal/mole (22,321 cm^{-1}) would be available. All of the single molecule and double molecule oxygen excitations shown in Figure 1 now have been observed in absorption (gaseous oxygen, 2200 psi, 6.5-cm cell, 20°), and all of the states have now been observed in solution chemiluminescence except the $2[^1\Sigma_g^+]$ state. We believe that this state is also excited, but is masked in our system by Cl_2 absorption. The $2[^1\Sigma_g^+]$ state corresponds to an energy of 75.1 kcal/mole (26,246 cm^{-1}) or up to 83.1 kcal/mole (29,069 cm^{-1}) with 2 quanta of vibrational excitation. The molecular oxygen states offer literally a stepladder of energy levels from which energy transfer can occur to acceptor molecules.

The early observations by Mallet[8] suggest to us that sensitized chemiluminescence is a probable mechanism in chemiluminescence reactions; he reported strong chemiluminescence of anthracene, acridine, eosin, fluorescein, quinine sulfate, and aesculin when these substances were present in the solution reaction $H_2O_2 + OCl^-$. More recent observations by Stauff, *et al.*,[9] Vassil'ev,[10] and Chandross[11] also favor an energy-transfer excitation of various acceptor molecules, in our view. In all of these cases, the luminescence observed is of the *unaltered* acceptor molecule. A striking example of such a chemiluminescence is that of zinc tetraphenylporphine studied by Linschitz,[12] in which the very narrow fluorescence band of the unaltered molecule is observed during an oxidation reaction carried out by tetralin hydroperoxide.

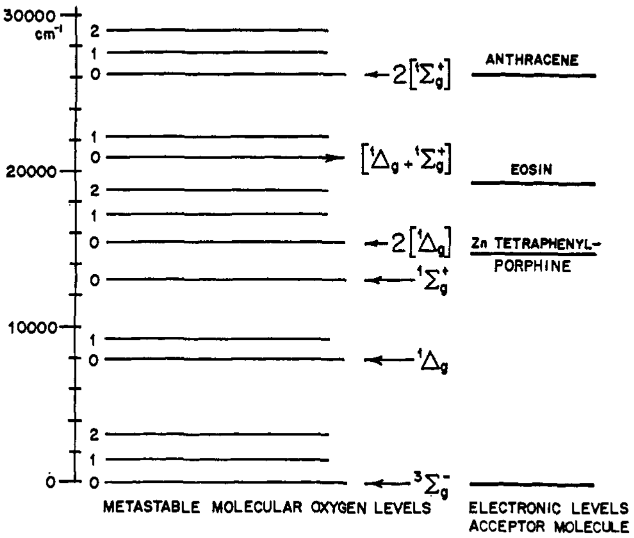

Figure 1. Electronic energy levels of molecular oxygen and excited singlet molecular oxygen dimers available for energy transfer in chemiluminescence (horizontal arrows label the pure electronic states).

In the inorganic reaction of the type $H_2O_2 + OCl^-$, the mechanism we proposed[2] for the solution reaction accounts for the production of double molecule excited states. In the red chemiluminescence from benzoyl peroxide thermally decomposing in benzene, studied by Bowen and Lloyd,[13] the double molecule states must be produced by the collisional approach and interaction of the two excited singlet oxygen molecules. The extreme prohibition of the oxygen singlet → triplet (g → g) transition results in extraordinary metastability of singlet excited oxygen.

In summary, we propose that *in systems generating excited (singlet) molecular oxygen, luminescence of any energetically favorable species may be produced and observed as a "chemiluminescence" by a direct energy transfer from excited oxygen molecular pairs.* The following observations lend support to this thesis: (a) the chemiluminescence spectrum is usually analogous to the fluorescence spectrum of the unaltered precursor molecule;[14] (b) the chemiluminescence of the acceptor molecule shows a square dependence on the peroxide of oxygen concentration;[12,15] and (c) the extremely low quantum yields of chemiluminescence indicate that the luminescence is probably a minor side effect compared with the gross stoichiometry of the main oxidation reaction.

The quantum yield of chemiluminescence by an acceptor molecule may be much higher than the quantum yield of luminescence by molecular oxygen species in solution, depending on the relative rates of energy

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transfer *vs.* quenching of the excited oxygen;[16] vibrationally excited electronic states could be involved if the rate of energy transfer is greater than the vibrational relaxation rate.

Although there is now extensive evidence that O_2 does not dimerize in the ground state,[17] our chemiluminescence spectra[2] for the emission from the $2[^1\Delta_g]$ state and the corresponding absorption data indicate probable dimer formation in the interaction of two excited singlet molecules, indicated by the highly abnormal Franck–Condon intensities in these spectra compared with the single molecule transitions.

A detailed presentation of our numerous types of spectral data and a more meticulous analysis of the interpretation will be submitted for publication shortly in another place.

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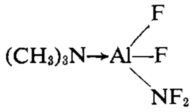
Received January 15, 1966

The Chemistry of Alane. VI. Preparation of an Aluminum Difluoramide from Trimethylamine Alane and Difluoramine

Sir:

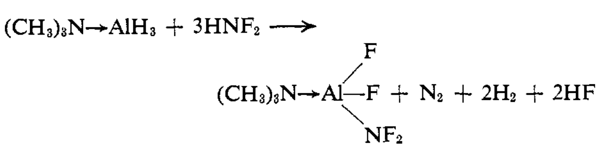
We wish to report the preparation of a new aluminum–fluorine compound (1) in which a difluoramino group is attached to aluminum.



$$(CH_3)_3N\rightarrow Al(F)_2(NF_2)$$

I

To our knowledge this is the first example of a compound containing a difluoramino group bonded to a metal atom. The synthesis of I was accomplished by the reaction shown in eq 1. Trimethylamine alane[1] (2.4 mmoles) in 10 ml of dry tetrahydrofuran was added to a solution of 8 mmoles of difluoramine[2] in 20 ml of dry tetrahydrofuran kept at −23° under an argon atmosphere. The reaction media became yellow and slowly precipitated a white, crystalline solid.



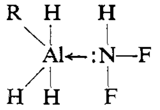
$$(CH_3)_3N\rightarrow AlH_3 + 3HNF_2 \longrightarrow (CH_3)_3N\rightarrow Al(F)_2(NF_2) + N_2 + 2H_2 + 2HF \quad (1)$$

I

The solid, which was isolated by filtration and dried *in vacuo*, weighed 0.35 g (95% yield). Gas evolution amounting to 5.8 mmoles (80% of theory) was observed during the reaction. The gas was collected in a buret over mercury and subjected to qualitative mass spectral analysis. Nitrogen and hydrogen were observed in addition to solvent and argon. No trace of HNF_2, N_2F_2, or N_2F_4 were detected in the evolved gas. The solid (I) dissolved readily in water without apparent gas evolution to yield a solution capable of oxidizing starch–iodide paper. The infrared spectrum of I displayed strong N–F absorptions at 10.25, 10.5–10.8, and 11.55 μ and was devoid of bands in the 5–6 μ region, indicating the absence of Al–H bonds. Treatment of I with sulfuric acid generated some difluoramine which was detected by mass spectrometry. Hot alkali quantitatively liberated trimethylamine from I.

Anal. Calcd for $C_3H_9AlF_4N_2$: C, 20.46; H, 5.15; N, 15.91; $(CH_3)_3N$, 33.57. Found: C, 20.62; H, 5.26; N, 15.60; $(CH_3)_3N$, 34.60.

A similar reaction was attempted between difluoramine and lithium aluminum hydride in dry 1,2-dimethoxyethane. However, this reaction proceeded with extreme vigor and could not be controlled so that no useful products were isolated. In contrast, lithium borohydride in dry 1,2-dimethoxyethane did not react with difluoramine. This marked difference in reactivity between the aluminum hydrides and lithium borohydride may be explained by the fact that aluminum can expand its octet, while boron cannot. Thus, reactions of tetracoordinate aluminum may involve the intermediate



$$R(H)_3Al\leftarrow :NH(H)F_2$$

(where R = H^- or Me_3N), which then loses hydrogen to form the covalent Al–N bond. This initial intermediate cannot be formed in the case of tetracoordinate boron.

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January 8, 1966

Intermolecular Isomerization of a Thiocyanatopalladium(II) Complex to Its Isothiocyanato Linkage Isomer

Sir:

Recent communications report the detection of the unstable linkage isomers $[(NC)_5CoNC]^{3-}$,[1] $[(H_2O)_5CrNC]^{2+}$,[2] and $[(H_2O)_5CrSCN]^{2+}$.[3] These complexes were prepared *in situ* and their solution chemistry was examined, but their salts were not isolated.

Because of this interest in linkage isomers of metal complexes, we wish to report the preparation of the SCN^- and PF_6^- salts of $[(Et_4dien)PdSCN]^+$ and the kinetics and mechanism of isomerization of this complex.[4]

$$[(Et_4dien)PdSCN]^+ \longrightarrow [(Et_4dien)PdNCS]^+ \quad (1)$$

The reaction between $K_2[Pd(SCN)_4]$ and Et_4dien in the cold yields the unstable S-bonded isomer $[(Et_4dien)PdSCN]SCN$. To a solution containing 1 g of $K_2[Pd(SCN)_4]$ in 10 ml of acetone at −10° was added 2 ml of

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