

Figure 1. ESR spectra of VO^{2+} and VO^{2+} -ATP in aqueous solution. Concentrations are all $\sim 10^{-2}$ M. Room temperature spectra are at ~ 9.5 GHz; spectra at 77°K are at ~ 9.1 GHz: (a) VO^{2+} at room temperature, $A = 116$ G; (b) VO^{2+} and ATP at room temperature, $A = 114$ G; (c) VO^{2+} at 77°K ; (d) VO^{2+} and ATP at 77°K , $A_{\parallel} = 200$ G, $A_{\perp} = 76$ G.

hydrolysis. When H_2O_2 is present in a limited amount ($[\text{H}_2\text{O}_2] = 10^{-3}$ M, $[\text{VO}^{2+}] = [\text{ATP}] = 10^{-2}$ M) the production of P_i slows after 2×10^{-3} M P_i is produced, and reverts to the rate of hydrolysis observed in runs without H_2O_2 present. This indicates that oxidation of $\text{VO}^{2+} \rightarrow \text{V}(\text{V})$ is the important factor in enhancement of ATP hydrolysis.

Replacement of H_2O_2 with MnO_4^- also yields enhancement of ATP hydrolysis. Replacement of ATP with $\text{P}_2\text{O}_7^{4-}$ also inhibits oxidation of VO^{2+} by H_2O_2 with hydrolysis of $\text{P}_2\text{O}_7^{4-}$ to P_i .

ESR spectra of VO^{2+} (with and without ATP) are shown in Figure 1. No ^{31}P superhyperfine structure is observed. At room temperature, the normal eight-line ^{51}V signal (a) is broadened upon addition of ATP (b). At 77°K , the line broadening present for ATP-free VO^{2+} (c) is diminished and the g -anisotropy of the ^{51}V hyperfine structure is revealed (d). All these facts clearly indicate that binding occurs between VO^{2+} and ATP in aqueous solution.

When H_2O_2 and VO^{2+} are added in equimolar concentrations (without ATP), the solution becomes amber and then exhibits the bright yellow of the decavanadate ion ($\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$) permanently.⁸

When ATP is present, addition of equimolar quantities of VO^{2+} and H_2O_2 results in a solution which is initially amber in color, and then reverts to the blue VO^{2+} color. Thus, when ATP is present, VO^{2+} is not immediately oxidized as it is without ATP. ESR monitoring shows that VO^{2+} is being oxidized slowly. Thus, ATP protects the VO^{2+} from oxidation by H_2O_2 . Only after about 1 week does the solution exhibit the yellow decavanadate color. At this

point, the hydrolysis of ATP is essentially complete. Gas evolution is observed and becomes more prevalent as the $[\text{VO}^{2+}]_0/[\text{ATP}]_0$ ratio is increased above 1/1 and as $[\text{H}_2\text{O}_2]_0$ is increased.

A large excess of H_2O_2 added to a VO^{2+} -ATP solution causes it to turn amber, then pale yellow-green. ESR spectra indicate that some VO^{2+} is still present, so that ATP is still protecting the VO^{2+} to some extent.

In runs in which $[\text{VO}^{2+}] = [\text{H}_2\text{O}_2]$, and in which ATP was present, only $\sim 50\%$ of the VO^{2+} was oxidized, as shown by the intensity of the ESR spectrum. Brooks and Sicilio⁷ observed similar behavior and explained it by saying that some of the H_2O_2 undergoes catalytic decomposition to O_2 and H_2O .

They also report that the rate of oxidation is slowed 100-fold by the introduction of chelating agents like EDTA^{4-} . ATP chelation in the present study slows the rate of oxidation by a factor of $\sim 10^3$ or more. $\text{P}_2\text{O}_7^{4-}$ exhibits a similar but smaller inhibition.

The structure of the VO^{2+} -ATP complex probably involves phosphate O's bound to three of the five available coordination positions with the adenosine moiety folded over and probably bound to one or both of the other available sites, resulting in shielding of the VO^{2+} ion from attack by H_2O_2 .

If direct H_2O_2 oxidation of VO^{2+} is prevented by the chelated ATP, it is possible that H_2O_2 attacks at the phosphate linkage of the ATP ligand (bound to VO^{2+}), followed by electron transfer from the VO^{2+} ion through the phosphate to the H_2O_2 . This would explain the large catalytic effect the redox process has on the hydrolysis of ATP.

Detailed kinetic studies on this and other redox systems are now under way to determine the mechanistic pathways involved in the enhancement of ATP hydrolysis by electron transfer reactions. It is hoped that such studies will provide insights concerning the enzymatic catalysis of ATP hydrolysis in biological systems.

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Crossed Molecular Beam Synthesis of a New Compound, CH_3IF

Sir:

The crossed molecular beam technique, while primarily confined to elucidating the dynamics of reactions for which the products are readily predicted, offers a method for the

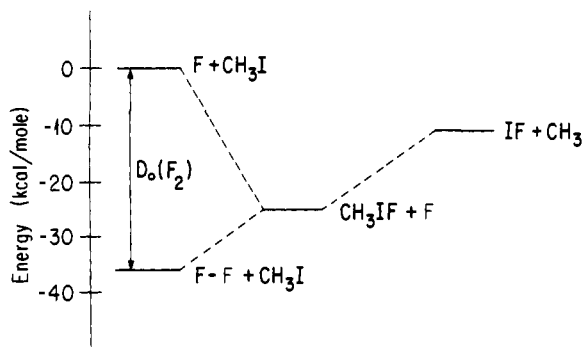


Figure 1. Energetics of reactions of atomic and molecular fluorine with CH_3I .

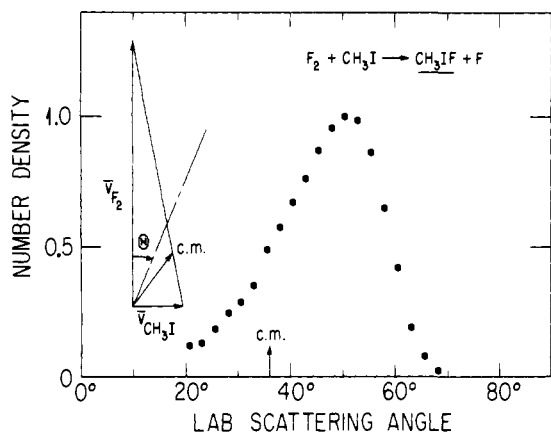


Figure 2. CH_3IF laboratory angular distribution. $\bar{E} = 25.1$ kcal/mol. Velocity vector Newton diagram is also shown.

gas phase synthesis of compounds normally not isolable in the laboratory. Many crossed molecular beam studies of reactions of halogen atoms with homonuclear and heteronuclear halogen molecules^{1,2} and organic compounds^{3,4} indicate the existence of long-lived collision complexes whose stabilities must be tens of kilocalories per mole relative to reactants. Although a knowledge of the structure and stability of these complexes is vital in understanding the dynamics of their unimolecular decompositions to product fragments, very little information is available concerning the stabilities of these "molecules."

A recent crossed molecular beam study of the reaction of atomic fluorine with methyl iodide, to produce $\text{IF} + \text{CH}_3$ has been shown to proceed through a long-lived collision complex as inferred from center of mass angular distribution symmetry.⁵ If a statistical model is applicable to the decomposition of the complex, such a model predicts that the collision complex CH_3IF in which F is bound to I must be stable by at least 20–30 kcal/mol relative to CH_3I and F.⁶

In this communication we report direct observation of the compound CH_3IF produced in the endoergic reaction of molecular fluorine with CH_3I . The relationship between the energetics of the atomic and molecular reactions of fluorine with CH_3I is shown in Figure 1. Theoretically, if CH_3IF is tens of kilocalories per mole more stable than CH_3I and F, the CH_3IF molecule should be formed either through termolecular association of CH_3I and F or through the endoergic bimolecular reaction of CH_3I and F_2 . The CH_3IF molecule, the isolation of which would be difficult, has not been observed to date. The stability of CH_3IF relative to reactants is not only of utmost importance in understanding the reaction dynamics of $\text{F} + \text{CH}_3\text{I}$ but also presents an interesting problem in chemical bonding.

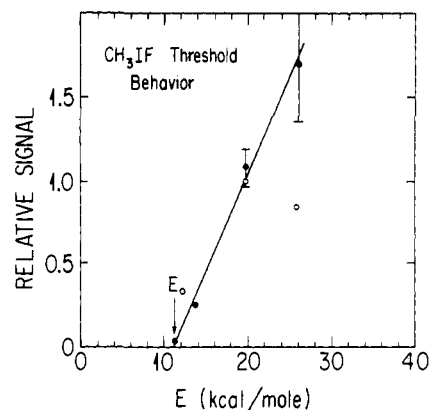


Figure 3. Energy dependence of relative total cross section for CH_3IF production. Closed circles denote data corrected for F_2 dissociation; open circles denote uncorrected data.

The experimental apparatus used in the production of CH_3IF has been described in detail elsewhere.^{5,7} The supersonic fluorine beam was produced by expanding a mixture of 2% F_2 –98% He through a nickel oven resistively heated up to 800° where $\sim 30\%$ dissociation occurs. The CH_3IF product (m/e 161), formed by the reaction of undissociated F_2 in the source, is detected every 2.5° in the laboratory, and the data are shown in Figure 2.

Although full kinematic analysis has not been completed for this system, a consideration of the data in conjunction with the velocity vector Newton diagram indicates that the CH_3IF products are scattered predominately into the backward hemisphere with respect to the incoming F_2 molecule.

The stability of the I–F bond in CH_3IF relative to the value of 68 kcal/mol for the diatomic molecule IF ⁸ is of interest and a study of the threshold behavior for CH_3IF production was carried out by detecting the CH_3IF product as a function of collision energy. Collision energies were controlled by adjusting the fluorine oven temperature. Figure 3 shows the energy dependence of the in-plane relative total cross section and extrapolation of the data to a threshold of 11 kcal/mol. The observed threshold combined with the dissociation energy of F_2 yields a lower bound on the IF bond strength in CH_3IF as 25 ± 3 kcal/mol.

The prominent peaks in the CH_3IF mass spectrum are found at m/e 161 (CH_3IF^+), m/e 160 (CH_2IF^+), m/e 146 (IF^+), m/e 34 (CH_3F^+), and m/e 33 (CH_2F^+) with approximate relative abundances 1:0.7:1:0.03:0.2 obtained at an electron energy of 200 eV.

The existence of this compound based upon the well-known polyvalency of iodine is not surprising especially in view of recent discussions of the stability of trihalogen systems with an iodine atom in the center,^{1,9,10} although the IF bond stability is unexpectedly large. The observation of this compound suggests that a wide variety of such compounds involving interhalogen bonding can be produced by endoergic bimolecular reactions using high energy molecular beams, and the lower bounds of binding energies of the new compounds can be obtained by careful investigation of the threshold energy of formation and their structures determined by matrix isolation experiments or molecular beam resonance spectroscopy.

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An Unusual Inverse Primary Deuterium Isotope Effect. Factors Operating in the Tunneling Mechanism of Chromium(VI) Oxidation of Alcohols

Sir:

In an earlier article¹ it has been shown through application of the temperature dependent isotope effect criterion (TIC) that typical alcohol oxidations with Cr(VI) proceed through the decomposition of an initially formed chromate ester in a pericyclic transition state of H transfer (Figure 1a). Moreover, abnormal cases involving steric hindrance or highly electron withdrawing substituent effects² take place via a quantum mechanical tunneling process, (Figure 1b).

Lee and Stewart³ report that the value of k_H/k_D declines with increasing acidity of the medium. These authors have advanced the interpretation that a change in mechanism is induced by $[H^+]$, so that at $k_H/k_D = 1$ the rate determining step is the formation of chromate ester rather than its decomposition in which H transfer is occurring. However, in view of the demonstration¹ that k_H/k_D in the abnormal cases is determined by both TIC parameters, $[(\Delta E_a)_D^H$ and $A_H/A_D]$, an alternative interpretation involving hydrogen tunneling may be considered. This explanation can be reasoned from the fact that the associated water structure involved in the asymmetric H-transfer mechanism depicted in Figure 1b is strongly influenced by the presence of acidic components of the medium and from the fact that this type of transition state structure may be implicated in quantum mechanical tunneling attending the "proton jump" transport⁴ mechanism.

This possibility has now been investigated in the case of the sterically hindered alcohol di-*tert*-butylcarbinol which exhibits direct evidence of undergoing, at least in part, the tunneling mechanism formulated in Figure 1b. The results, indeed show that the TIC parameters for its Cr(VI) oxidation are sensitively dependent on $[H^+]$. Table I summarizes the data derived from nearly 100 kinetic runs correlated in Arrhenius relationships encompassing temperature ranges of >20 to $>50^\circ$. Product identification was carried out for each reaction acidity, using gas chromatographic analysis. In each case, only the "normal" (di-*tert*-butyl ketone) product was detected along with unreacted and unreacted

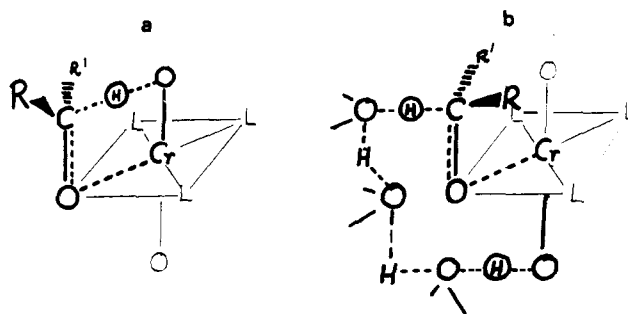


Figure 1. Critical bonds are represented by heavy lines; L = ligand structures; R, R' = alkyl or aryl.

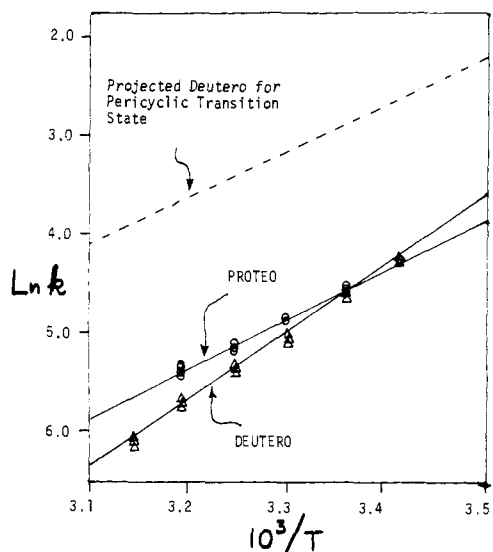


Figure 2. Inverse isotope effect on the rates of Cr(VI) oxidation of di-*tert*-butylcarbinol in 5.9 M perchloric-acetic acid medium as a function of absolute temperature.

ranged di-*tert*-butylcarbinol. Figure 2 is presented to illustrate the conclusion that, at a specific $[H^+]$, the TIC parameters have magnitudes which produce $k_H/k_D = 1.0$ at *ca.* 25° . At other $[H^+]$ the isotope effect disappears only at much greater temperatures in correspondence to variations of the TIC parameters with acidity. Furthermore, significant inverse isotope effects (for example, $k_H/k_D = 0.8$, Figure 2) are realized at near-ambient temperatures (35°) with no visible signs of mechanistic change in the pattern of Cr(VI) oxidation, *i.e.*, no curvature or discontinuities in the Arrhenius relationships.⁵

The data in Table I also reveal that the TIC parameters do not vary in a linear manner with acidity, although the isotope effect at 25° is shown to decrease with increasing acidity. This observation is consistent with the results of Lee and Stewart for substituted 2-propanols.³ An increase from 0.1 to 3.5 M in $[H^+]$ produces a *ca.* 100-fold increase in A_H/A_D and a reduction of 1.8 kcal in $(\Delta E_a)_D^H$; a further increase from 3.5 to 5.9 M in $[H^+]$ is attended by a steep decline (by a factor of 350) in A_H/A_D and an increase of 2.4 kcal in $(\Delta E_a)_D^H$. Such excursions (in opposite phase) of the magnitudes of $(\Delta E_a)_D^H$ can be interpreted to reflect the partitioning between tunneling and pericyclic transition states of oxidation, as $[H^+]$ influences the associated water structure and its ability to participate in the essential H-transfer mechanism of Figure 1b.

Traditionally, kinetic isotope effects are extrapolated to⁵ or reported at ambient temperatures; such (single) values are applied as criteria for the identification of rate determining steps in H-transfer mechanisms. In general, it may