tomycin C.[11] It is not clear why the use of a lesser amount of $Na_2S_2O_4$ favors the formation of compound II and it will therefore be of interest to examine if the generation of compound II requires a one-electron reduction, while perhaps the generation of I requires a two-electron reduction.[12] Experiments to study these questions and to elucidate the structures of the other products formed together with I and II are in progress.

The facile formation and isolation of compounds I and II lead us to propose that the use of potassium ethylxanthate in preference to other nucleophiles may be advantageous for investigating other suggested bioreductive alkylating agents.[13]

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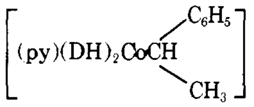
Metal-Alkyl Bond Dissociation Energies in Organocobalt Compounds Related to Vitamin B_{12} Coenzymes

Sir:

Transition metal-alkyl bond dissociation energies are of importance in the context of various homogeneous catalytic processes,[1,2] as well as certain biochemical systems, notably those encompassing the coenzyme B_{12} (5′-deoxyadenosylcobalamin) dependent rearrangements.[3-5] The "strengths" of transition metal-alkyl bonds and the contributions of thermodynamic and kinetic factors to the "stabilization" of such bonds have been issues of some controversy in recent years.[6] Unfortunately, hardly any transition metal-alkyl bond dissociation energies are known reliably, nor have general methods for the determination of such energies been developed.[7]

We describe here an effective new approach to the determination of certain transition metal-alkyl bond dissociation energies and its application to the first direct estimation of cobalt-carbon bond dissociation energies in some organocobalt compounds of possible relevance as coenzyme B_{12} analogues.

Our studies relate to the determination of the equilibrium constants and kinetics of reactions exemplified by eq 1 (where



$$\left[(py)(DH)_2CoCH(CH_3)C_6H_5\right]$$

1

$$\rightleftarrows [(py)(DH)_2Co^{II}] + C_6H_5CH{=}CH_2 + \tfrac{1}{2}H_2 \qquad (1)$$

2

DH_2 = dimethylglyoxime and py = pyridine) which we have found to attain a readily measurable equilibrium at ambient temperatures under H_2 pressures of ~1 atm. Reactions, corresponding to the reverse of eq 1 and analogues thereof (including variants involving the addition of "cobalt hydrides" to activated olefins), have long been recognized as synthetic routes to organocobalt compounds, including organocobalamins.[8-11] The decomposition of alkyl-cobalt compounds to yield olefins also is well-documented qualitatively,[9,12,13] but neither the *equilibrium nor kinetic behavior* of reactions such as eq 1 appears to have previously been examined.

Solutions of $[(py)(DH)_2CoCH(CH_3)C_6H_5]$ in toluene, equilibrated with a constant partial pressure of H_2, decomposed according to eq 1, attaining a measurable equilibrium in ~1 h at ~20 °C. The approach to equilibrium was monitored, and the final equilibrium concentrations of **1** and **2** were determined, spectrophotometrically. Identical results were obtained monitoring either the absorbance decrease at 360 nm ($\epsilon(\mathbf{1})$ 9.55×10^3, $\epsilon(\mathbf{2})$ 3.6×10^3 M^{-1} cm^{-1}) or the absorbance increase at 430 nm ($\epsilon(\mathbf{1})$ 2.1×10^3, $\epsilon(\mathbf{2})$ 3.5×10^3 M^{-1} cm^{-1}). The value of the equilibrium constant, K_2 (defined by eq 2), at 18.8 °C was determined to be $(6.4 \pm 0.2) \times 10^{-6}$ $M^{3/2}$ and was found to be unaffected by initial concentration variations over the following ranges: $[(py)(DH)_2CoCH(CH_3)C_6H_5]$, 1.1×10^{-4} to 3.0×10^{-4} M; $[H_2]$, 8.5×10^{-4} to 2.6×10^{-3} M (0.32 to 1.0 atm of H_2);[14] excess [py], 0 to 2×10^{-3} M. The same value of the equilibrium constant was determined when the equilibrium was approached from the reverse direction, i.e., starting from $[(py)(DH)_2Co^{II}]$, $C_6H_5CH{=}CH_2$, and H_2. Values of K_2, determined at temperature ranging from 9.8 to 37.0 °C, are listed in Table I.[15] These data yield an excellent linear van't Hoff plot (log K vs. T^{-1}) corresponding to $\Delta H° = 22.1 \pm 0.5$ kcal/mol and $\Delta S° = 51.9 \pm 1.6$ cal/(mol deg).

$$K_2 = \frac{[(py)(DH)_2Co^{II}][C_6H_5CH{=}CH_2][H_2]^{1/2}}{[(py)(DH)_2CoCH(CH_3)C_6H_5]} \qquad (2)$$

Using the above value of $\Delta H°$ for reaction 1, in combination with available data for the heats of formation of $C_6H_5CH{=}CH_2$ ($\Delta H_f°$ (25 °C) = 35.2 kcal/mol)[16] and of the $C_6H_5\dot{C}HCH_3$ radical ($\Delta H_f°$ (25 °C) = 33 kcal/mol),[17] the cobalt-carbon bond dissociation energy of $[(py)(DH)_2Co—CH(CH_3)C_6H_5]$ can be deduced to be 19.9 kcal/mol using the following thermochemical cycle:

$$\begin{array}{lrr} & \Delta H^\circ & \\ [(\mathrm{py})(\mathrm{DH})_2\mathrm{CoCH(CH_3)C_6H_5}] \rightleftarrows [(\mathrm{py})(\mathrm{DH})_2\mathrm{Co^{II}}] + \mathrm{C_6H_5CH{=}CH_2} + \tfrac{1}{2}\mathrm{H_2} & 22.1 & (3) \\ \mathrm{C_6H_5CH{=}CH_2} + \tfrac{1}{2}\mathrm{H_2} \rightleftarrows \mathrm{C_6H_5\dot{C}HCH_3} & -2.2 & (4) \\ \hline [(\mathrm{py})(\mathrm{DH})_2\mathrm{CoCH(CH_3)C_6H_5}] \rightleftarrows [(\mathrm{py})(\mathrm{DH})_2\mathrm{Co^{II}}] + \mathrm{C_6H_5CHCH_3} & 19.9 & (5) \end{array}$$

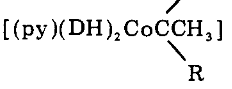
It should be noted that this determination of the cobalt-carbon bond dissociation energy rests entirely upon thermodynamic considerations and is *independent of the mechanism of reaction 1*. However, it is noteworthy that the value so determined (19.9 kcal/mol) is close to the value (21.2 kcal/mol) of the enthalpy of activation of reaction 1, deduced from kinetic measurements *in the absence of* H_2 (i.e., under an atmosphere of N_2). Under these conditions reaction 1 (monitored spectrophotometrically, the formation of H_2 being confirmed mass spectrometrically) goes to completion according to the first-order rate law, eq 6. Kinetic measurements over the temperature range 14-35 °C yielded the value $k_6(25\ °\mathrm{C}) = 7.8 \times 10^{-4}\ \mathrm{s}^{-1}$; $\Delta H^{\ddagger}_6 = 21.2 \pm 0.5$ kcal/mol; $\Delta S^{\ddagger}_6 = -1.4 \pm 1.5$ cal/(mol deg).

$$-\mathrm{d}[(\mathrm{py})(\mathrm{DH})_2\mathrm{CoCH(CH_3)C_6H_5}]/\mathrm{d}t = k_6[(\mathrm{py})(\mathrm{DH})_2\mathrm{CoCH(CH_3)C_6H_5}] \quad (6)$$

A plausible (but not unequivocal[13]) mechanistic interpretation of reaction 1, depicted by eq 7 and 8, involves homolytic

$$[(\mathrm{py})(\mathrm{DH})_2\mathrm{CoCH(CH_3)C_6H_5}] \xrightarrow{k_6} \{[(\mathrm{py})(\mathrm{DH})_2\mathrm{Co^{II}}] + \mathrm{C_6H_5CHCH_3}\} \xrightarrow{\text{fast}} [(\mathrm{py})(\mathrm{DH})_2\mathrm{CoH}] + \mathrm{C_6H_5CH{=}CH_2} \quad (7)$$

$$[(\mathrm{py})(\mathrm{DH})_2\mathrm{CoH}] \xrightarrow{\text{fast}} [(\mathrm{py})(\mathrm{DH})_2\mathrm{Co^{II}}] + \tfrac{1}{2}\mathrm{H_2} \quad (8)$$



$$[(\mathrm{py})(\mathrm{DH})_2\mathrm{CoC(R)(R')CH_3}] \longrightarrow [(\mathrm{py})(\mathrm{DH})_2\mathrm{Co^{II}}] + \mathrm{CH_2{=}C(R)R'} + \tfrac{1}{2}\mathrm{H_2} \quad (9)$$

dissociation of the cobalt-alkyl bond as the rate-determining step. It has been established in various studies[18-22] that the reverse of this step, i.e., the coupling of organic radicals with low-spin cobalt(II) complexes, proceeds at rates close to diffusion controlled (and hence with very small activation barriers). Accordingly, this interpretation predicts, in agreement with the above findings, that $\Delta H^{\ddagger}$ for reaction 1 should be close to the cobalt-carbon bond dissociation energy. The study of the kinetics of reactions analogous to eq 1 thus provides another approach to the determination of metal-alkyl bond dissociation energies.[23] Preliminary studies confirm that such reactions do occur for a variety of secondary alkyl bis(dimethylglyoximato)cobalt compounds (eq 9, where R = H, and R′ = CH_3, n-C_6H_{13}, $C_6H_5CH_2$, and where R = CH_3 and R′ = CN), with first-order kinetics (i.e., analogous to eq 6) and with $\Delta H^{\ddagger}$ values ranging from 20 kcal/mol (for $CoC(CH_3)_2CN$) to 33 kcal/mol (for $CoCH(CH_3)CH_2C_6H_5$).

Qualitative comparisons (e.g., of benzylcobalamin and benzylbis(dimethylglyoximato)cobalt compounds) suggest that the cobalt-carbon bond dissociation energies in organocobalamins are lower than those in corresponding organobis(dimethylglyoximato)cobalt compounds. It thus appears likely that the cobalt-carbon bond dissociation energies of alkylcobalamins, including coenzyme B_{12}, do not exceed the range of 20-30 kcal/mol yielded by our measurements on organobis(dimethylglyoximato)cobalt compounds. Qualitative support for this is provided by observations concerning the stability of benzylcobalamin. Attempts to prepare benzylcobalamin by conventional synthetic routes involving the reactions of either vitamin B_{12s}[24] or B_{12r}[25] with benzyl bromide did yield spectroscopic evidence for its initial formation in solution. However, benzylcobalamin proved to be too unstable for isolation and decomposed within a few hours, bibenzyl being among the products of decomposition. If this decomposition is assumed to be due to benzyl-cobalt bond homolysis, the rate (assuming $\Delta S^{\ddagger} \sim 0$) would correspond to an activation enthalpy of ~15-20 kcal/mol. Identifying this value with the benzyl-cobalt bond dissociation energy and assuming the usual difference of ~5-10 kcal/mol between benzyl- and unactivated alkyl-bond dissociation energies[17] would, accordingly, imply a value in the range of 20-30 kcal/mol for the cobalt-carbon bond dissociation energies of coenzyme B_{12} and other primary alkylcobalamins.[26] This is quite compatible with the proposed role of coenzyme B_{12} as a 5′-deoxyadenosyl radical precursor, very little additional activation being required for homolysis of such a weak bond to occur at rates consistent with those of coenzyme B_{12} dependent enzymic processes.

Table I. Equilibrium Constants of Reaction 1 in Toluene

temp, °C	10^6K_2, $M^{3/2}$	temp, °C	10^6K_2, $M^{3/2}$
9.8	1.77	23.8	10.1
15.6	3.46	24.5	12.4
18.8	6.40	31.0	28.9
21.2	8.14	37.0	59.9

We are presently attempting to extend these approaches to the estimation of cobalt-alkyl bond dissociation energies in other organocobalt compounds including organocobalamins.

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(23) The facile occurrence of the H-abstraction step, i.e., the second stage of reaction 7, which serves to "trap" the initially produced $C_6H_5\dot{C}HCH_3$ radical irreversibly and inhibit reversal of the first step, finds precedent in earlier studies on other low-spin cobalt(II) complexes, e.g., $[Co(CN)_5]^{3-}$ + $R\dot{C}HCH_3 \rightarrow [HCo(CN)_5]^{3-} + RCH{=}CH_2$. The competition between this process and the alternative combination reaction, $[Co(CN)_5]^{3-} + R\dot{C}HCH_3 \rightarrow [R(CH_3)CHCo(CN)_5]^{3-}$, is favored for secondary (i.e., $(CH_3)_2\dot{C}H$) relative to primary (e.g., $CH_3\dot{C}H_2$) radicals.[18]

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(26) One of the few transition metal-alkyl bond dissociation energies to have been directly determined, i.e., that of $CH_3Mn(CO)_5$ (~30 kcal/mol), also lies in this low range.[27] The "weakness" of transition metal-alkyl bonds thus appears to be fairly widespread.

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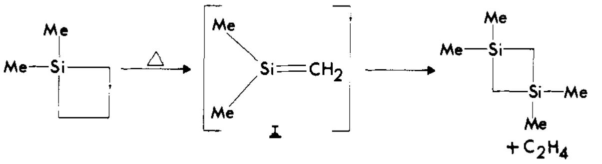
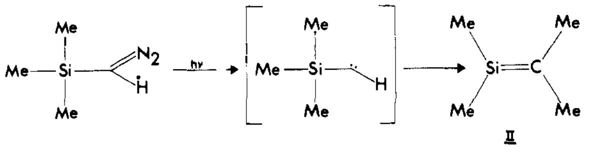
Heat of Formation of 1,1-Dimethylsilaethylene by Ion Cyclotron Resonance Spectroscopy

Sir:

Interest has time and again focused upon the generation and characterization of molecules containing formal carbon-silicon double bonds.[1,2] For example, the existence of 1,1-dimethylsilaethylene (I), as an intermediate in the pyrolysis reaction (1), has been suggested[2a] and the rate interpreted to yield a heat of formation of 12-29 kcal mol^{-1} for the species.[2d,3] Mass spectral evidence supporting the existence of I in the gas phase has only recently been advanced.[2w] The low-temperature matrix infrared spectra of both 1,1-dimethylsilaethylene (I)[5a,b] (obtained from the pyrolysis reaction 1) and 1,1,2-trimethylsilaethylene (II)[5c,d] (obtained upon photolysis of trimethylsiladiazomethane, reaction 2) have been recorded. Close parallels between the infrared spectrum of the silaethylene and that of trimethylethylene have been drawn[5b] and suggest the overall similarity of the geometrical structures of the two molecules. Although there exist no further experimental structural data to substantiate or contest such an interpretation, the best available molecular orbital calculations on parent silaethylene indicate a planar geometry with a barrier to rotation of 46 kcal mol^{-1},[6,7] which may be compared with the corresponding theoretical barrier of 64 kcal mol^{-1} for rotation in ethylene[6] (experimentally, the activation energy required for cis/trans isomerization of 1,2-dideuteroethylene is 65 kcal mol^{-1} [8]). These data provide some indication of the relative π-bond strengths of the two molecules.[9]



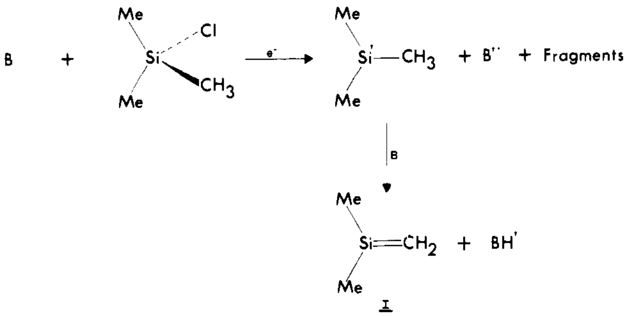
(1)



(2)

We describe in this communication a direct experimental determination of the heat of formation of 1,1-dimethylsilaethylene (I), and indirectly of its carbon-silicon π-bond strength, by ion cyclotron resonance (ICR) spectroscopy.[10]

Scheme I



Our experimental procedure is outlined in Scheme I.[11] Trimethylsilyl chloride, a base (B) of known strength and an inert buffer gas (Ar or Kr) are added to an ICR spectrometer in approximate ratio of 2:1:50-100 and total pressure on the order of 10^{-5} Torr. Electron impact results in the initial production of trimethylsilyl cation (via rapid halide loss from the radical cation of trimethylsilyl chloride) and, depending on base B, of $B^{+\cdot}$ and of fragment ions of B. If base B is sufficiently strong, it will be capable of proton abstraction from the trimethylsilyl cation, giving rise to an ion of mass corresponding to BH^+ and concurrently to the neutral molecule 1,1-dimethylsilaethylene. Therefore, by employing a series of abstracting bases of known and increasing strength, and by monitoring the onset of production of BH^+ (verified by standard double resonance techniques[10,11a] to arise from the trimethylsilyl cation), it is possible to determine an approximate enthalpy for deprotonation of the silicon-centered cation. Piperidine (enthalpy of proton transfer 21.9 kcal mol^{-1} greater than that of the ammonia standard)[12] was the strongest base considered which was not observed to abstract a proton from trimethylsilyl cation; the weaker bases, ethylmethylamine (19.4 kcal mol^{-1}) and trimethylamine (21.2 kcal mol^{-1}), did not result in proton abstraction. Isopropylethylamine ($\Delta H°$ of protonation 23.4 kcal mol^{-1} above NH_3) was the weakest base for which proton abstraction was observed; the stronger bases di-*n*-propylamine (23.9 kcal mol^{-1}) and diisopropylamine (26.0 kcal mol^{-1}) also lead to proton abstraction. These results were unaffected by further addition of buffer gas.

We conclude, therefore, that the proton affinity of 1,1-dimethylsilaethylene is >21.9 kcal mol^{-1} (relative to ammonia) but <23.4 kcal mol^{-1}. The average of these two relative values (22.7 kcal mol^{-1}), combined with the absolute enthalpy of protonation of ammonia (205 kcal mol^{-1})[13] and the heats of formation of trimethylsilyl cation (160 kcal mol^{-1})[14] and of H^+ (367.2 kcal mol^{-1}),[15] yields a value 20.5 kcal mol^{-1} for the heat of formation of 1,1-dimethylsilaethylene.

Three sources of error are easily identified. The first concerns the finite resolution of the gas-phase proton-affinity scale and the likelihood that slightly endothermic proton-transfer reactions as well as thermoneutral and exothermic processes will occur and will be detected. We suspect uncertainties on the order of ±1 kcal mol^{-1} in our measurement and interpretation of the threshold for proton abstraction from the trimethylsilyl cation due to these causes. Further uncertainty arises due to the requirement of an absolute basis for the proton-affinity scale. The absolute proton affinity of our standard, ammonia, is at present not completely certain, with estimates ranging from a low of 203 kcal mol^{-1} to a high of 207 kcal mol^{-1}.[13] Finally deduction of $\Delta H_f°$ for 1,1-dimethylsilaethylene requires a heat of formation for its precursor, the trimethylsilyl cation. The value that we have employed, 160 kcal mol^{-1},[14] derives from appearance potential measurements and is conceivably in error by as much as 2 kcal mol^{-1}.

Our experimental value for the heat of formation of 1,1-dimethylsilaethylene of 20.5 kcal mol^{-1} is consistent with the

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