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Dehydrohalogenation by Complex Base. Preferential Loss of "Poorer" Halogen Leaving Groups

Sir:

In olefin formation by base-promoted dehydrohalogenation, an order of leaving group reactivity of I > Br > Cl ≫ F has been observed on several occassions.[1,2] This is the normal trend expected for the operation of a leaving group "element effect"[3] in a concerted E2 mechanism. We report a reversal of this leaving group ordering for syn eliminations from *trans*-1,2-dihalocycloalklanes promoted by "complex base".

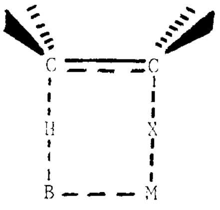
Caubere[4] has reported a surprising propensity for a mixture of $NaNH_2$–NaO-*t*-Bu, "complex base," to induce syn eliminations from *trans*-1,2-dibromocycloalkanes (C_5–C_7). Thus, when treated with $NaNH_2$–NaO-*t*-Bu in THF at room temperature, *trans*-1,2-dibromocyclohexane yielded 60% 1-bromocyclohexene and 36% cyclohexene. Under the same conditions, neither $NaNH_2$ nor NaO-*t*-Bu gave significant amounts of 1-bromocyclohexene. This method is now the preferred synthetic route to several 1-bromocycloalkenes.

In an attempt to gain mechanistic insight into this reaction, we have investigated complex base promoted eliminations from *trans*-1,2-dihalocyclohexanes which contain two different halogen atoms. Reaction of *trans*-1-bromo-2-chlorocyclohexane with $NaNH_2$–NaO-*t*-Bu in THF at room temperature for 24 h yielded 52–55% 1-bromocyclohexene and 30–31% 1-chlorocyclohexene.[5,6] Dehydrohalogenation involving the "poorer" leaving group is preferred. This tendency was further accentuated in reactions of *trans*-1-bromo-2-fluorocyclohexane and *trans*-1-chloro-2-fluorocyclohexane with complex base under the same conditions.[5,6] The former dihalide gave an 85% yield of 1-bromocyclohexene and the latter an 85% yield of 1-chlorocyclohexene. No 1-fluorocyclohexene was detected in either elimination. Thus, dehydrofluorination occurs in preference to dehydrochlorination or dehydrobromination in these complex base promoted syn eliminations.[7] This is particularly striking in view of the forcing conditions required to induce dehydrofluorination from alkyl fluorides.[1,9,10]

Reaction of *trans*-1-bromo-2-chlorocyclopentane with $NaNH_2$–NaO-*t*-Bu in THF at room temperature for 20 h produced 50% 1-bromocyclopentene and 38% 1-chlorocyclopentene. Similarly, treatment of *trans*-1-chloro-2-bromoacenaphthene with complex base in THF at 0 °C[11] for 5 h yielded 54% 1-bromoacenaphthylene and 42% 1-chloroacenaphthylene. These results demonstrate that the preference for syn dehydrochlorination over syn dehydrobromination with complex base is not limited to six-membered-ring dihalides.

The preferential loss of "poorer" halogen leaving groups in complex base promoted eliminations is confined to reactions with syn stereochemistry. Treatment of 1-bromo-1-chlorocyclohexane and *cis*-1-bromo-2-chlorocyclohexane with $NaNH_2$–NaO-*t*-Bu in THF at room temperature for 16 and 12 h,[5] respectively, produced 99% yields of 1-chlorocyclohexene. Only traces of 1-bromocyclohexene were detected. Therefore, complex base promoted anti eliminations from 1,1- and *cis*-1,2-dihalocyclohexanes exhibit the same preference for dehydrobromination over dehydrochlorination noted with more ordinary base-solvent combinations.[12] This result suggests an E2 mechanism for dehydrohalogenations involving complex base, but with some special interactions for syn eliminations.

The facilitation of concerted syn elimination by ion-paired bases has been explained using the cyclic transition state **1**.[13,14]



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In this transition state, the metal cation, M, simultaneously coordinates with the base, B, and the leaving group, X. Our current observations may be readily rationalized if, for syn eliminations promoted by complex base, the strength of interaction between X and M becomes the dominant leaving group property rather than the customary preeminence of the C–X bond strength. Because of its high electronegativity favoring strong interactions with M, fluoro would be the preferred halogen leaving group. Similarly, the chloro leaving group should be removed in preference to bromo.

Further aspects of the mechanistic and synthetic features of complex base promoted 1,2 eliminations are in progress.

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hexane, 3:3:2) were magnetically stirred under nitrogen. Product analysis was by gas chromatography using appropriate internal standards.
(6) Only traces of cyclohexene were observed. 1-Halocyclohexenes are partially converted to unknown products under these reaction conditions. Nevertheless the observed high (83–88%) 1-halocyclohexene yields indicate that product instability is not a serious problem.
(7) Dialkyl α-bromo-α′-fluorosuccinates eliminate hydrogen fluoride in preference to hydrogen bromide when treated with potassium acetate in 50% aqueous methanol or ethanol.[8] However, kinetic studies revealed the reaction to be complex and its mechanism remains unknown.
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Relatively Low-Temperature Thermochemical Generation of Molecular Hydrogen from Decomposition of Water by Platinum. Red-Light Photochemical Origin of the Chlorophyll a Water Splitting Reaction

Sir:

The concept of free-energy storage in solar conversion has in recent years focused on the cleavage of water

$$2H_2O \rightarrow 2H_2 + O_2 \quad \Delta G° = 56.7\ \text{kcal/mol} \qquad (1)$$

by heat[1,2] and by visible light.[3,4] The thermochemical generation of hydrogen from water cleavage is limited by the temperature and product removal requirements of reaction 1.[1,2] It is known that Pt is oxidized to yield hydroxides and oxides in the presence of air and water.[5,6] In earlier studies workers investigated[6] the corrosion of Pt in the presence of O_2 and H_2O at ordinary temperatures, and reported that no H_2 was evolved.[6a] However, it was unclear whether hydrogen would be evolved from the thermochemical reaction of Pt with H_2O, in the absence of O_2, at temperatures comparatively lower than those required for the thermal cleavage of water in reaction 1.[1,2] In this communication we describe experiments that delineate the effects of heat and visible light on Pt in deoxygenated water. We report the observation of hydrogen evolution when Pt and water were heated at relatively low temperatures in the range of 130–210 °C. In sharp contrast with the water photolysis results we obtained on illuminating platinized Chl a,[4] no significant amounts of oxygen were detected in the thermochemical Pt-H_2O reaction. No molecular hydrogen and oxygen were detected when Pt in water was illuminated in the visible wavelength region.

Shiny Pt foils were cleaned in aqua regia and flamed over a methane-oxygen torch. Platinization of Pt was accomplished by passing a 30-mA current for 15 min through a 7×10^{-2} M chloroplatinic acid solution containing 6×10^{-4} M lead acetate. The platinized foil was rinsed with distilled water and inserted in a Pyrex cell containing doubly distilled water deoxygenated with Ar gas for 30 min. The sample cell consisted of two sections connected by O-ring joints. Each section was made of 10-mm (o.d.) glass tubing, the lower one being constructed with a glass frit on which the sample was placed, and through which the Ar gas was passed during the degassing of the water. A Kontes 4-mm Kel-F high-vacuum valve was attached to the lower and upper end of the cell assembly to maintain the gas tightness of the system. For application in gas chromatographic analyses, the extreme upper tip of the cell was fitted with another O-ring joint to an evacuation chamber enclosed by a rubber septum through which the gaseous sample was withdrawn into a 100-μL Anspec Pressure-Lok syringe for transfer into a Carle 8700 basic gas chromatograph equipped with a dual thermistor detector and a 2.4-m 80/100 mesh molecular sieve 5A column activated at 300 °C for 4 h in an He gas stream. Argon was used as the sample carrier gas. In mass spectrometric work, the cell was assembled with a ground-glass joint at its upper tip to allow direct attachment to the gas inlet chamber of the mass spectrometer. In light experiments the Pt electrode was irradiated with 4-W, all lines, from a Coherent Radiation Model 53 CW Argon ion laser or with the entire output of a 1000-W tungsten-halogen lamp. In thermal reactions the Pt-H_2O assembly was heated at temperatures up to 210 °C. The mass spectrometric measurements were made using a Consolidated Electrodynamics Corp. 21-110-B mass spectrometer. In the Hersch method[7] for detecting H_2 and O_2, the evolved H_2 gas is determined by burning the hydrogen in a stream of oxygen carried by gaseous He. The level of background O_2 in the He flow was registered as a current amplified by a Keithley 427 current amplifier using the Hersch O_2 indicator constructed in this laboratory.

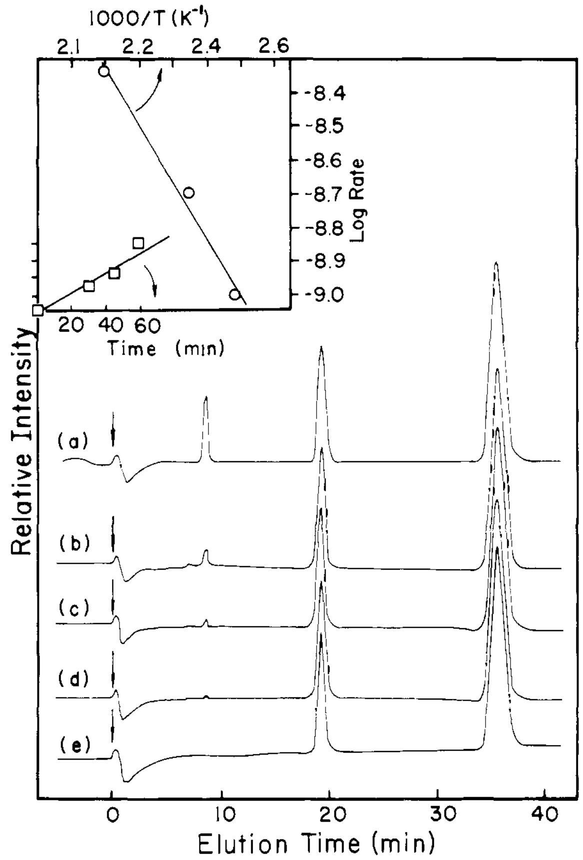

Figure 1. Gas chromatographic determination of hydrogen evolution in the Pt-H_2O reaction: (a) generation of 8×10^{-8} mol of H_2 by passing a 4-mA current for 4 s; (b–d) H_2 generated by heating doubly distilled water at 205 °C in the presence of a platinized Pt foil ($0.8 \times 1.2 \times 0.02$ cm^3) for 60, 45, and 30 min, respectively; (e) gas chromatogram of sample after 1-h irradiation with Ar ion laser. The arrows indicate the time of sample introduction into the gas chromatograph. The position of the hydrogen peak in a provides definitive evidence for the presence of H_2 from the Pt-H_2O reaction. The electrolysis experiment also permits sample calibration. Air leakage through the rubber septum in the evacuation bulb during sample transfer was responsible for the oxygen and nitrogen peaks at 19 and 35 min, respectively. The temperature and time dependences of the hydrogen evolution rate is shown in the inset. The time dependence data points correspond to b–d. The points in the Arrhenius plot were obtained at 205, 155, and 130 °C. The slope of this plot yields an activation energy of 3.48 kcal mol^{-1}.