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Crossed Molecular Beam Measurement of the Intrinsic Activation Barrier for the Endoergic Reaction $\text{Hg} + \text{I}_2 \rightarrow \text{HgI} + \text{I}$

Sir:

We report an accurate experimental determination of the threshold energy for a neutral atom-diatomic molecule exchange reaction. From this measurement and the known endoergicity of the reaction the intrinsic activation barrier is directly obtained.¹

We have studied the endoergic reaction of ground state Hg atoms with I_2 in the vicinity of the reaction threshold via the crossed molecular beam technique. Based on the experimental threshold energy the intrinsic activation barrier has been determined to be essentially zero (within 1 kcal mol^{-1}). This experimental result is to be contrasted with the substantial barrier energies (usually tens of kilocalories) inferred for many gas phase reactions from bulk kinetic studies.

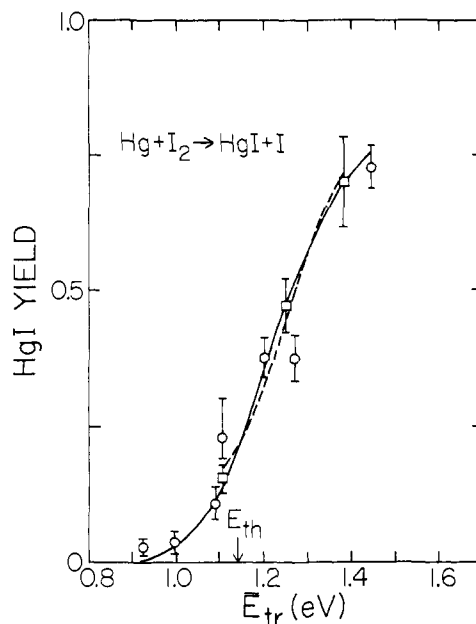


Figure 1. Translational energy dependence of the yield of HgI. Circles and squares denote data sets with different distributions of reactants' translational energy. The solid and dashed curves are the calculated fits (see text) to the circles and squares, respectively, using the "best" experimental (translational) threshold $E_{th} = 1.14 \text{ eV}$, indicated by the arrow.

The HgI product from the reactive scattering of a seeded supersonic nozzle beam of Hg by a beam of I_2 was measured. The yield of scattered HgI was determined at ten values of the average collision energy, \bar{E}_{tr} , from 0.9 to 1.5 eV, and was found to increase monotonically with translational energy over this range.² The reaction threshold energy was then determined through comparison of the experimental reactive yield with that calculated by convoluting an Arrhenius (line-of-centers) cross section functionality with the known distribution of reactants' relative kinetic energy (at each \bar{E}_{tr}). The results of two separate series of experiments are displayed in Figure 1. This procedure leads to a total energy threshold for reaction of $1.18 \pm 0.03 \text{ eV}$. Since the endoergicity of the reaction is $\Delta E_0^\circ = 1.15 \pm 0.01 \text{ eV}$ (using the recently reevaluated $D_0(\text{HgI}) = 0.39 \pm 0.01 \text{ eV}^3$), this result implies an intrinsic activation barrier of $0.03 \pm 0.03 \text{ eV}$.

This study of the reactive scattering of Hg by I_2 is an extension of previous work⁴ in this laboratory, in which the elastic scattering of the same system was investigated. The apparatus is essentially unchanged. Briefly, it consists of a supersonic nozzle beam of Hg (1 Torr) seeded in a variable excess (70–150 Torr) of H_2 , a crossed beam of iodine from a multichannel array source (363 K), and a rotatable (in-plane) detector, which includes a high efficiency electron bombardment ionizer, quadrupole mass filter, and a channel electron multiplier operated in the pulse-counting mode. The mercury atoms are accelerated to hyperthermal velocities (most-probable speed, $v_{m.p.}$, in the range $1200\text{--}1600 \text{ m s}^{-1}$). The velocity distribution of each of the ten mercury beams was measured via the time-of-flight (TOF) technique with a beam monitor consisting of an electron bombardment ionizer and a quadrupole mass filter mounted opposite the nozzle beyond the main scattering chamber. The velocity distribution of the I_2 ($v_{m.p.} = 245 \text{ m s}^{-1}$) was measured with this monitor placed opposite the array. The distribution of relative kinetic energy is thereby experimentally determined for each value of \bar{E}_{tr} at which scattering is observed.

The angular distribution of the HgI scattered in the plane of the incident beams is measured at each experimental energy. The distributions are essentially isomorphic, exhibiting peaks at lab angles of about 10° with respect to the Hg beam. An-

gular widths increase from 20° to 50° with increasing translational energy. The experimental in-plane yield (HgI number density signal per unit density of reactant Hg and I₂) is determined by integration of the angular distributions.

The determination of the threshold energy for an endoergic reaction depends upon a very accurate knowledge of the distribution of relative translational energy and its convolution of the actual cross section functionality.⁵ Each angular distribution is fit by convoluting an assumed center-of-mass detailed differential cross section with the known relative velocity distribution. The predicted product yield is obtained by integrating these fits over the laboratory angles.⁶

The resulting experimental and calculated yields are presented as a function of the average relative translational energy in Figure 1, where the circles and squares represent data obtained from separate experimental series with two slightly different translational energy distributions. The experimental data are simulated by including in the differential cross section an Arrhenius translational energy dependence¹ with different values of the translational energy threshold, E_{th} . The value of E_{th} has been systematically varied to achieve a best fit to the data, shown in the figure with $E_{th} = 1.14$ eV.

Since the average internal energy of the I₂ beam is 0.04 eV, the total energy threshold for reaction is 1.18 ± 0.03 eV. As previously mentioned, the reaction has an inherent endoergicity $\Delta E_0^\circ = 1.15 \pm 0.01$ eV. Thus, the intrinsic activation barrier to the reaction is 0.03 ± 0.03 eV (95% C.L.), i.e., the barrier for the exoergic, reverse reaction of I with HgI is essentially zero (within 1 kcal mol⁻¹).

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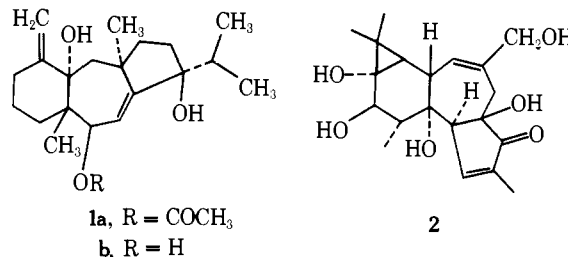
The Isolation and Structure of Dolatriol¹

Sir:

Marine Mollusca of the family Aplysiidae (class Gastropoda) are commonly known as sea hares.² The poisonous properties of sea hare secretions were already known in pre-Christian times. Indeed, such toxic materials are believed to have been used by Agrippina, mother of Nero (A.D. 37–70) to dispatch relatives blocking his ascent to Roman emperor. The poisonous aspects of an Indian Ocean sea hare were vividly recorded by Grevin in a French work of 1568.³ Recently, a toxic constituent of the sea hare *Stylocheilus longicauda* was designated aplysiatoxin and its structure was nicely elucidated by the Scheuer group.⁴ We have evaluated a small number of

such gastropods for antineoplastic constituents and have so far located four species⁵ giving extracts with confirmed level activity against the National Cancer Institute's murine P-388 lymphocytic leukemia (PS system). Of special interest has been the Indian Ocean (East Africa) *Dolabella auricularia*. Both ethanol and water extracts from this animal were found to be quite cytotoxic and markedly inhibit growth of the P-388 leukemia.

We now wish to report that careful chromatographic (prepacked Merck Size B silica gel 60 columns and elution with 70:0.3 heptane-acetone)¹ separation (guided by bioassay) of the ethanol extract has led to the first two members of a uniquely different class of diterpene. The new substances have been designated dolatriol 6-acetate (**1a**) and dolatriol (**1b**). Chromatographic fractions (4 ml volumes) 56–65 afforded (0.001% yield) dolatriol 6-acetate (**1a**, C₂₂H₃₄O₄, M⁺ 362 *m/e*) as large hexagonal needles (from heptane-acetone) melting at 210–212°: ir (KBr) 3570, 3439, 1733, 1638, and 899 cm⁻¹; ¹H NMR (CDCl₃) δ 0.85 (d, *J* = 7 Hz, 3 H, isopropyl methyl), 0.89 (s, 3 H, C-5 methyl), 1.03 (d, *J* = 7 Hz, 3 H, isopropyl methyl), 1.19 (s, C-12 methyl), 2.09 (s, acetyl methyl), 2.6 (m, 1 H, isopropyl methine), 4.78 (s, 1 H, C-7 H), 4.93 (s, 1 H, C-6 H), 5.28 (d, *J*_{ab} = 6 Hz, 1 H, methylene), and 6.16 (d, *J*_{ab} = 6 Hz, 1 H, methylene). Dolatriol (**1b**, C₂₀H₃₂O₃, M⁺ 320 *m/e*) was obtained (0.0005% yield from fractions 95–107) as fine needles, mp 235–236° from heptane-acetone and displayed: ir (KBr) 3500, 3410, 1638, and 909 cm⁻¹; ¹H NMR (CDCl₃) δ 0.78 (s, 3 H, C-5 methyl), 0.84 (d, *J* = 7 Hz, 3 H, isopropyl methyl), 1.01 (d, *J* = 7 Hz, 3 H, isopropyl methyl), 1.19 (s, 3 H, C-12 methyl), 4.73 (s, 1 H, C-7 H), 4.89 (s, 1 H, C-6 H), 4.97 (d, *J*_{ab} = 6 Hz, 1 H, methylene), and 5.45 (d, *J*_{ab} = 6 Hz, 1 H, methylene). Under acidic conditions dolatriol 6-acetate (**1a**) was readily converted to dolatriol.



A single crystal of dolatriol 6-acetate of suitable size was obtained by cleaving one of the hexagonal needles as obtained above. The observed Laue symmetry and extinctions correspond to the very unusual rhombohedral space group $R\bar{3}$ with: $a = 24.152$ (9), $c = 9.544$ (3) Å; $Z = 9$; $\rho_{calcd} = 1.124$ for C₂₂H₃₄O₄, $\rho_{obsd} = 1.12$ (2) g/cm³. Diffraction intensities were measured in the θ - 2θ scan mode using graphite monochromated Mo K α radiation on a Syntex P1 diffractometer; of the 2646 reflections examined ($\sin \theta/\lambda \leq 0.6497$), a total of 2020 unique reflections were retained with $|F_o| > 0$. No corrections were applied for either absorption or extinction.

The structure was readily solved by direct methods using the MULTAN-74 system of programs.⁶ Large block least-squares refinement⁷ of the structure with anisotropic thermal parameters and fixed hydrogen positions (234 independent variables in two blocks) yielded a standard residual $R = 0.1297$ for the 1897 strongest reflections; a weighted residual $R_w = (\sum_w (|F_o| - |F_c|)^2 / \sum_w |F_o|^2)^{1/2}$ of 0.0865 was obtained with $w = 1/\sigma_F^2$. Many of the hydrogen atoms, including those on both hydroxyl groups, were observed in a difference synthesis based on a refined anisotropic model; for the final refinement both O-H atoms were placed as found and all C-H atoms were placed at idealized positions.