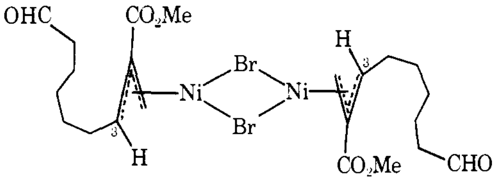

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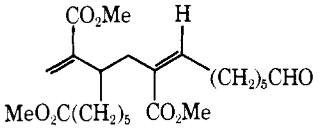

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isomers of **2**. The consistent formation **11a** from both **2a** and **2b** suggests a common allyl-zinc intermediate and a common π-allylnickel intermediate (perhaps **12**);[25] this stereoselectivity also allows confidence that the model studies can be applied to total synthesis of natural products which bear the α-methylene-γ-lactone unit fused to a perhydroazulene skeleton in the cis geometry.[6,26]

References and Notes

(1) Cf. P. A. Grieco, *Synthesis*, 67 (1975).
(2) Examples of recent interest include vernolepin[3,4] and isotelekin.[5]
(3) S. M. Kupchan, R. J. Hemingway, D. Werner, A. Karim, A. T. McPhail, and G. A. Sim, *J. Am. Chem. Soc.*, **90**, 3596 (1968).
(4) Cf. P. A. Grieco, J. Noguez, and Y. Masahi, *Tetrahedron Lett.*, 4213 (1975), and references therein.
(5) R. B. Miller and E. S. Behare, *J. Am. Chem. Soc.*, **96**, 8102 (1974).
(6) Natural products with the α-methylene-γ-lactone fused to a seven-membered carbocyclic ring include a variety of perhydroazulene derivatives. For a few examples including biological testing results, see ref 1 and 7. For a more complete listing of more than 30 examples, see T. K. Devon and A. I. Scott, "Handbook of Naturally Occurring Compounds", Vol II (Terpenes), Academic Press, New York, N.Y., 1972.
(7) S. M. Kupchan, M. A. Eakin, and A. M. Thomas, *J. Med. Chem.*, **14**, 1147 (1971).
(8) Complex structures containing ten-membered carbocyclic rings such as elephantopin[9] have potent biological activity,[7] and have not yet been successfully synthesized.
(9) S. M. Kupchan, Y. Aynehchi, J. M. Cassady, A. T. McPhail, G. A. Sim, H. K. Schnoes, and A. L. Burlingame, *J. Am. Chem. Soc.*, **88**, 3674 (1966).
(10) Cf. S. M. Kupchan, D. C. Fessler, M. A. Eakin, and T. J. Giacobbe, *Science*, **168**, 376 (1970).
(11) Prepared from cycloheptanone in 65% yield overall via ozonolysis of 1-acetoxycycloheptene to give methyl 7,7-dimethoxyheptanoate. Then hydride reduction followed by selective oxidation (CrO_3/pyridine) produced 7,7-dimethoxyheptanal (**3**).
(12) J. L. Herrmann and R. H. Schlessinger, *Tetrahedron Lett.*, 2429 (1973).
(13) Cf. A. Löffler, R. J. Pratt, H. P. Rüesch, and A. S. Drieding, *Helv. Chim. Acta*, **53**, 383 (1970).
(14) For discussions, see (a) D. J. Faulkner, *Synthesis*, 175 (1971); (b) S. F. Brady, M. A. Ilton, and W. S. Johnson, *J. Am. Chem. Soc.*, **90**, 2882 (1968).
(15) J. C. Depezay and Y. L. Merrer, *Tetrahedron Let.*, 2751, 2755 (1974).
(16) E. J. Corey, H. A. Kirst, and J. A. Katzenellenbogen, *J. Am. Chem. Soc.*, **92**, 6314 (1970).
(17) This compound was prepared by hydride reduction of methyl 6,6-dimethoxyhexanoate[18] which, in turn, was obtained from ozonolysis of 1-acetoxycyclohexene; the overall yield from cyclohexanone was 88%.
(18) C. D. Hard and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **74**, 5324 (1952)
(19) Prepared according to R. M. Blankenship, K. A. Burdett, and J. S. Swenton, *J. Org. Chem.*, **39**, 2300 (1974).
(20) A few examples of intramolecular Reformatsky-type reactions are known, but none involving formation of homoallylic alcohols. Cf. Table V in M. W. Rathke, *Org. React.*, **22**, 423 (1975).
(21) Intermolecular examples of reactions closely related to the conversion **2** → **11** have been reported: E. Ohler, K. Reininger, and U. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **9**, 457 (1970).
(22) Comparisons were made directly with spectra of **11a** and **11b** kindly provided by Professor J. A. Marshall. Comparisons of chemical shift data with those quoted in the literature can be misleading; the absorptions due to the exocyclic methylene unit in the ^{1}H NMR spectra show substantial solvent (CCl_4 vs. $CDCl_3$) and concentration effects. The most reliable distinguishing features of the ^{1}H NMR spectra are the shapes of the envelopes in the region δ 1.8–3 due to the aliphatic $-CH_2-$ units.
(23) For convenient preparations, see (a) M. F. Semmelhack, *Org. React.*, **19**, 178 (1972); (b) R. A. Schunn, *Inorg. Synth.*, **13**, 124 (1973).
(24) The reaction of allylic halides with bis(1,5-cyclooctadiene)nickel is a general, mild method for formation of π-allylnickel halide complexes: G. Wilke et al., *Angew. Chem., Int. Ed. Engl.*, **5**, 151 (1966).
(25) The reaction of π-allylnickel halide complexes with aldehydes has been reported: (a) E. J. Corey and M. F. Semmelhack, *J. Am. Chem. Soc.*, **89**, 2755 (1967); (b) L. S. Hegedus, S. D. Wagner, E. L. Waterman, and K. Siirala-Hansen, *J. Org. Chem.*, **40**, 593 (1975). The latter reference includes intermolecular examples closely related to the conversion **2** → **11** using zerovalent nickel reagents.
(26) We are grateful to the National Institutes of Health for generous financial support (Grant AI-08687).
(27) Recipient of a Camille and Henry Dreyfuss Teacher-Scholar Award, 1973–1978.

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On the Entropic Control of Chemiluminescent Reactions

Sir:

Perrin has discussed the efficiency of chemiluminescent reactions from a thermodynamic point of view and concluded that in some systems there must be a "thermodynamic control" which puts a limit to the emission quantum yield.[1] This conclusion was based on the analysis of a cycle that would otherwise transform heat into work, violating the second principle. We consider that the proposed cycle really shows that a chemiluminescent reaction cannot be employed to transform heat into work and not that the reaction cannot take place with a high quantum yield. Let us consider the cycle proposed by Perrin[1]

Step i: The chemiluminescent reaction

$$A \rightarrow B + h\nu \tag{1}$$

takes place isothermally at a temperature T.

Step ii: The radiation emitted in step i enters a Carnot machine that produces an amount of work W_{max} and converts some of the energy into heat (which goes to a reservoir at temperature T); and

Step iii: Work is employed to regenerate A in the reaction

$$B \rightarrow A$$

which also takes place at temperature T.

If we define

$$\Delta G = \bar{G}_B - \bar{G}_A$$

the second principle requires that, for the first step

$$-\Delta G \geq N_{Av} h\nu - TS_R \tag{2}$$

where S_R is the entropy associated with the radiation.[2]

For the machine, the maximum work obtainable is given by

$$W_{max} = N_{Av} h\nu (T_e - T)/T_e \tag{3}$$

where T_e is the temperature associated to the radiation.[2] If we consider that

$$S_R = N_{Av} h\nu / T_e \tag{4}$$

from eq 2 and 3 we obtain that

$$W_{max} \leq -\Delta G \tag{5}$$

This last equation shows that the maximum work obtainable is always less (or equal if all the processes were reversible) than the work required by step iii, even if the quantum yield of the chemiluminescent reaction is 1. Work must then be expended in running any real machine comprising this cycle. We can conclude then that, thermodynamics does not impose any control on the quantum yield of a chemiluminescent reaction. Thermodynamics, through eq 2, can determine if reaction 1 or reaction 6

$$B + h\nu \rightarrow A \tag{6}$$

is faster under a given set of experimental conditions (concentrations, temperature and density of the radiation field), but only kinetics can decide which of the two microscopic processes

$$\mathrm{A} \rightarrow \mathrm{B}^* \qquad (7)$$

followed by

$$\mathrm{B}^* \rightarrow \mathrm{B} + h\nu \qquad (8)$$

or

$$\mathrm{A} \rightarrow \mathrm{B} + \text{heat} \qquad (9)$$

is faster under a given set of experimental conditions.

The "intriguing question" posed by Perrin[1] (why wave functions, which are ignorant of entropy, nevertheless must be such as to avoid violating the laws of thermodynamics) does not appear if we differentiate the macroscopic behavior (controlled by the free energy reactants and products, including the radiation), from the kinetic microscopic behavior (controlled by the wave functions).

References and Notes

(1) Ch. Perrin, *J. Am. Chem. Soc.*, **97** 4419 (1975).
(2) M. D. Archer, VII International Conference on Photochemistry, Edmonton, 1975.

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Does the Second Law of Thermodynamics Restrict Chemiluminescent Reactions?

Sir:

Some chemiluminescent reactions emit photons with energies greater than the heat of reaction.[1] The literature[2-5] is confused as to whether thermodynamics restricts their rates or yields. We show below that (a) the restriction imposed by the second law on the rate (and hence on the brightness) is in a sense trivial because it leads to the normal rate expression of the transition state theory and (b) it imposes no limitation on quantum yields. Recent claims[2] and some earlier work[4] are therefore invalid, mainly through confusion of *rates* and *yields*.

Consider a simplified case. Assume only *one* reaction path. See Figure 1. Each chemical-electronic state has a manifold of vibration–rotation–translation states. Assume that B* is a singlet state and ignore any differences in vibrational frequencies, etc., between B and B*, so both states have the same entropy, $S°$.

Take A and B to be at unit activity, in amounts such that the reaction of 1 mol produces negligible change in the activities. All these conditions can be relaxed.[6]

Kinetically, the rate of emission, hence the reaction rate, is given by the steady-state concentration [B*] of the excited product times the unit rate of emission. The maximum [B*] is the equilibrium concentration with respect to the reaction A → B*. There will be both induced and spontaneous emission but, when B* is higher in free energy than A by several RT per mole, only the spontaneous process is important. The usual connection between the equilibrium constant [B*]/[A] and the standard free energy change $\Delta G°_{\mathrm{B^*A}} = G°_{\mathrm{B^*}} - G°_{\mathrm{A}}$ is

$$[\mathrm{B}^*] = [\mathrm{A}]e^{-\Delta G°_{\mathrm{B^*A}}/RT} \qquad (1)$$

The spontaneous emission rate is $8\pi\nu^2\sigma\mathcal{N}/c^2$ photons per second per Hertz per mole[7] where ν is the frequency of the emission (assumed here to have a narrow frequency range), σ is the absorption cross section for frequency ν, per molecule, $\mathcal{N}$ is Avogadro's number, and c the velocity of light. Consequently the maximum rate $R_{\mathrm{f}}(\max)$ is

$$R_{\mathrm{f}}(\max) = (8\pi\nu^2\sigma\mathcal{N}/c^2)e^{-\Delta G°_{\mathrm{B^*A}}/RT}[\mathrm{A}] \qquad (2)$$

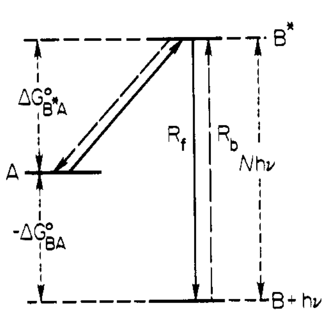

Figure 1. Reaction path A → B* → B + $h\nu$ showing forward and backward reactions and free energy differences.

If the standard entropy $S°$ of B* and B is approximately the same, then $G°_{\mathrm{B^*}} - G°_{\mathrm{B}} \cong \mathcal{N}h\nu$ since only the energy term is left (neglecting ΔPV). Then (see Figure 1)

$$\Delta G°_{\mathrm{B^*A}} = G°_{\mathrm{B^*}} - G°_{\mathrm{B}} + G°_{\mathrm{B}} - G°_{\mathrm{A}} = \mathcal{N}h\nu + \Delta G°_{\mathrm{BA}} \qquad (3)$$

Finally

$$R_{\mathrm{f}}(\max) = (8\pi\nu^2\sigma\mathcal{N}/c^2)e^{-(\Delta G°_{\mathrm{BA}}+\mathcal{N}h\nu)/RT} \qquad (4)$$

gives, at unit [A], the maximum forward rate, hence the rate of emission of photons, from a kinetic viewpoint.

Mayer[3] applied thermodynamics[8] to this process. The emitted photon has more energy than $-\Delta H_{\mathrm{BA}}$. Conservation of energy is no problem; heat can be drawn from the thermostat. The second law needs consideration since part of the light energy can be converted to work w and we know that $w \leq -\Delta G_{\mathrm{BA}}$. However, a device which converts light to work cannot be perfectly efficient. Consider a black body at temperature T_{e} in a heat bath at T_{e} and radiating a narrow band at ν through a filter to a converter at a lower temperature T_0. This is an engine converting heat from T_{e} partly to work and partly to heat at T_0. Hence its maximum efficiency is $(1 - T_0/T_{\mathrm{e}})$, the Carnot factor. The detector cannot tell the filtered black body radiation from any other source of the same surface, frequency, bandwidth, and brightness (i. e. photons per second per square centimeter). Therefore $(1 - T_0/T_{\mathrm{e}})$ is the maximum efficiency for converting light from any source to work, where T_{e} is the temperature of the black body which gives the same brightness at frequency ν. Thus,

$$w_{\max} = \mathcal{N}h\nu(1 - T_0/T_{\mathrm{e}}) = -\Delta G_{\mathrm{BA}} = -\Delta G°_{\mathrm{BA}} \qquad (5)$$

where the last step follows from the assumption of unit activities for A and B. For a black body the radiation density ρ (per hertz, say) is given by

$$\rho = \frac{(8\pi h\nu^3/c^3)}{e^{h\nu/kT_{\mathrm{e}}} - 1} \cong (8\pi h\nu^3/c^3)e^{-h\nu/kT_{\mathrm{e}}} \qquad (6)$$

when $h\nu > kT_{\mathrm{e}}$ as for visible light. Hence $\ln(\rho c^3/8\pi h\nu^3) = -h\nu/kT_{\mathrm{e}}$ and $[1 - (T_0/T_{\mathrm{e}})] = 1 + (kT_0/h\nu)\ln(\rho c^3/8\pi h\nu^3)$. Insertion of this in eq 5 above gives $\mathcal{N}h\nu[1 + (kT_0/h\nu)\ln(\rho c^3/8\pi h\nu^3)] = -\Delta G°_{\mathrm{BA}} = -\Delta G°_{\mathrm{B^*A}} + \mathcal{N}h\nu$ (see eq 3) or

$$\rho = (8\pi h\nu^3/c^3)e^{-\Delta G°_{\mathrm{B^*A}}/RT_0} = 2S/c \qquad (7)$$

gives the maximum photon density ρ and maximum brightness S compatible with the second law restriction. The maximum photon density will give maximum work and will occur under reversible conditions. To achieve these, surround the reacting system with perfect mirrors so that the photon density will build up until it produces sufficient photochemical back-reaction $h\nu + \mathrm{B} \rightarrow \mathrm{B}^*$ to make the rate R_{b} of this back-reaction just equal to that of the forward reaction $\mathrm{B}^* \rightarrow \mathrm{B} + h\nu$, but $R_{\mathrm{b}} = \rho\sigma c\mathcal{N}[\mathrm{B}]/h\nu$ where $\rho/h\nu$ is photon density and σ is absorption cross section, so all photons in cylinder of volume $c\sigma$ are absorbed by one molecule in unit time, etc. Therefore,