

but only kinetics can decide which of the two microscopic processes



followed by



or



is faster under a given set of experimental conditions.

The "intriguing question" posed by Perrin¹ (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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Received December 16, 1975

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 literature²⁻⁵ 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 claims² and some earlier work⁴ 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 $A \rightarrow B^*$. 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 $\Delta G^\circ_{B^*A} = G^\circ_{B^*} - G^\circ_A$ is

$$[B^*] = [A]e^{-\Delta G^\circ_{B^*A}/RT} \quad (1)$$

The spontaneous emission rate is $8\pi\nu^2\sigma\mathcal{N}/c^2$ photons per second per Hertz per mole⁷ 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 $R_f(\text{max})$ is

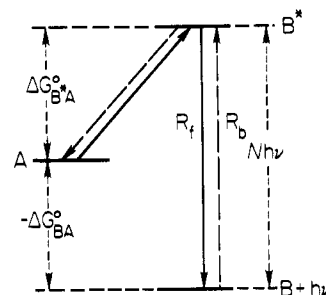


Figure 1. Reaction path $A \rightarrow B^* \rightarrow B + h\nu$ showing forward and backward reactions and free energy differences.

$$R_f(\text{max}) = (8\pi\nu^2\sigma\mathcal{N}/c^2)e^{-\Delta G^\circ_{B^*A}/RT}[A] \quad (2)$$

If the standard entropy S° of B^* and B is approximately the same, then $G^\circ_{B^*} - G^\circ_B \approx Nh\nu$ since only the energy term is left (neglecting ΔPV). Then (see Figure 1)

$$\Delta G^\circ_{B^*A} = G^\circ_{B^*} - G^\circ_B + G^\circ_B - G^\circ_A = Nh\nu + \Delta G^\circ_{BA} \quad (3)$$

Finally

$$R_f(\text{max}) = (8\pi\nu^2\sigma\mathcal{N}/c^2)e^{-(\Delta G^\circ_{BA} + Nh\nu)/RT} \quad (4)$$

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

Mayer³ applied thermodynamics⁸ to this process. The emitted photon has more energy than $-\Delta H_{BA}$. 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 $w \leq -\Delta G_{BA}$. 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 $(1 - T_0/T_e)$, 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 $(1 - T_0/T_e)$ 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,

$$w_{\text{max}} = Nh\nu(1 - T_0/T_e) = -\Delta G_{BA} = -\Delta G^\circ_{BA} \quad (5)$$

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

$$\rho = \frac{(8\pi h\nu^3/c^3)}{e^{h\nu/kT_e} - 1} \approx (8\pi h\nu^3/c^3)e^{-h\nu/kT_e} \quad (6)$$

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

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

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 $h\nu + B \rightarrow B^*$ to make the rate R_b of this back-reaction just equal to that of the forward reaction $B^* \rightarrow B + h\nu$, but $R_b = \rho\sigma c\mathcal{N}[B]/h\nu$ 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,

$$R_f(\max) = R_b = \rho \sigma c N / h \nu = (8\pi^2 \sigma N / c^2) e^{-\Delta G^\ddagger_{B^*A} / RT_0} \quad (8)$$

at unit [B]. This is identical with eq 4 obtained kinetically. Therefore, the second law does restrict the maximum brightness S_{\max} and the maximum forward rate R_f but only in the usual way that any activation energy slows a rate. We get no new restriction from these second law arguments that we would not have recognized from ordinary transition state kinetic arguments.

Next consider the quantum yield, defined to be the number of photons per molecule which reacts. By our hypotheses, this has to be unity, since it was postulated that there was only one path, so all molecules which react must follow that path and each must give one photon. In reality there will be other paths and a certain fraction of the reacting molecules will follow them. If these competitive paths give no light, the quantum yield will drop below unity. Without explicit knowledge of the rates of the alternate paths, it is impossible to say anything further about the quantum yield, even to bound it.

These arguments show that the application of the second law to chemiluminescent reactions does not introduce any restriction on the yield or any new restrictions on the rate which would not have been recognized from normal activation energy considerations.

Acknowledgment. This work was supported by NSF grant number CHE 76 00606.

References and Notes

- (1) See F. McCapra, *Q. Rev., Chem. Soc.*, **20**, 485 (1966).
- (2) C. L. Perrin, *J. Am. Chem. Soc.*, **97**, 4419 (1975).
- (3) J. E. Mayer in "The Luminescence of Biological Systems", F. H. Johnson, Ed., American Association for the Advancement of Science, Washington, D.C., 1955, p 48.
- (4) H. Eyring, ref 3, p 244.
- (5) W. Kauzmann, ref 3, p 251.
- (6) Thus triplet states, vibrational entropy effects, two product molecules, transition states higher than B^* , etc., could be accommodated.
- (7) For induced absorption see before eq 8 below and for emission/absorption see, for example, Pauling and Wilson, "Introduction to Quantum Mechanics", McGraw-Hill, New York, N.Y., 1935, p 301.
- (8) This section is a paraphrase of the treatment of Mayer, ref 3, and is also related closely to ref 5.

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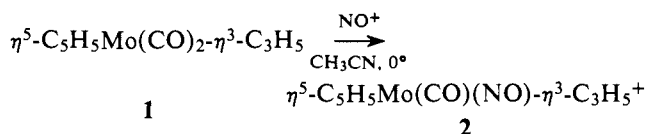
Received January 21, 1976

Conformational Interconversion in the Formation of η^5 -Cyclopentadienyl- η^3 -allyl-molybdenum Carbonyl Nitrosyl Cations

Sir:

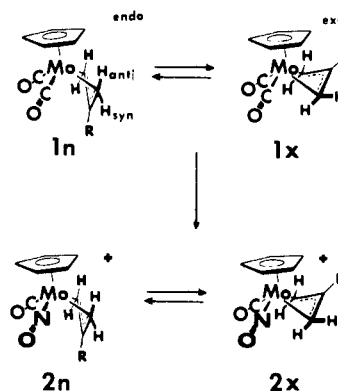
The susceptibility of ligands to nucleophilic attack is greatly enhanced when the complex is cationic.¹ Thus η^5 - $C_5H_5Fe(CO)_2$ (olefin) cations are readily subject to attack by nucleophiles,² whereas neutral species, such as η^5 - $C_5H_5Fe(CO)(SnR_3)$ (olefin) are not.³ Chirality as well as a localized charge can be introduced into complexes of this type by replacing CO with NO^+ .⁴ These reactions may be extended to chiral η^3 -allyl complexes, which are potential sources of chiral stereospecifically substituted olefins.⁵

These η^5 - $C_5H_5Mo(CO)(NO)-\eta^3$ - C_3H_5 derivatives can be prepared on a large scale in high yield by reaction of the readily available dicarbonyl η^3 -allyl complexes^{6,7} with 1 equiv of $NOPF_6$ in acetonitrile at 0° .

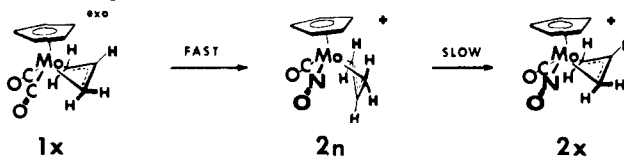


The reaction of η^5 - $C_5H_5Mo(CO)_2(NO)$ with allyl bromide/ $AgPF_6$ to produce complex **2** has been reported,⁸ but the synthesis shown above provides ready access to a large number of substituted derivatives.

NMR studies suggest that **2** undergoes an intramolecular rearrangement which interconverts conformers arising from two orientations of the η^3 -allyl moiety with respect to the η^5 -cyclopentadienyl ring. This behavior is analogous to that observed in **1**,⁶ which exists in solution as an equilibrium mixture of exo and endo conformers ($K_{exo/endo} = 4.7$, 0° , CD_3CN). At equilibrium the conformer ratio for the nitrosyl derivative, **2**, is approximately 5.2 (0° , $(CD_3)_2CO$).



Carbonyl displacement from **1** is extremely rapid ($t_{1/2} < 5$ s) and **2** is formed predominantly as one isomer (>85%). Two sets of syn and anti proton resonances are observed for each isomer as a consequence of the chirality at the metal.⁹ Upon standing, the weaker ABCDX pattern grows in intensity and the original intense resonances shrink to 14% as the system approaches equilibrium. By analogy with **1**, the endo isomer of **2** should be less stable thermodynamically and tend to convert to the exo isomer. These intensity changes are interpreted as a kinetically controlled predominance of the endo isomer in the initial product followed by a gradual approach to an equilibrium in which the exo isomer is favored.¹⁰ Thus, the principal path should be as follows.



It is noteworthy that the establishment of endo-exo equilibrium is over a million times faster in **1** than in **2**; i.e., the half-life at 0° is $\sim 10^{-1}$ s for **1** and $\sim 10^6$ for **2**.

Summarizing the kinetics below: two extremes which account for the reversal of conformer ratios between reactant and initial product are apparent based on the relative rates of reaction with NO^+ vs. conformational interconversion of **1**.

