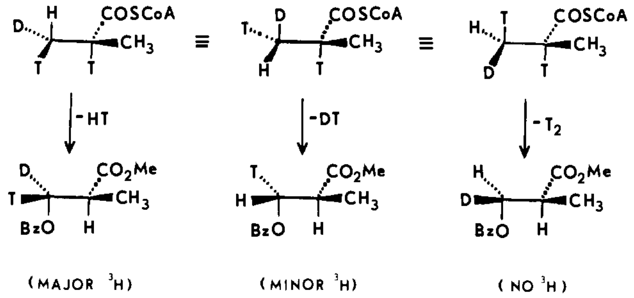
Scheme II[a]



[a] Predicted ^{3}H labeling patterns of metabolites from 7a for anti elimination of hydrogens from C-2 and C-3 of isobutyryl CoA (followed by syn hydration on *re,re* face of double bond, loss of CoA, and preparation of methyl ester benzoate).

Figure 1b shows the ^{1}H-decoupled ^{3}H NMR spectrum of **3b** obtained from the **7a** + **9a** isobutyrate mixture. Tritium signals at δ 5.80 (3-*pro-S* H) and 5.96 (3-*pro-R* H) result from the metabolism of the 2-*pro-S* chiral methyl of **7a** whereas the signal at δ 1.74 is derived from the unoxidized 2-*pro-R* chiral methyl of **9a**. The ^{3}H chemical shifts correspond closely with the analogous proton signals in Figure 1a. The relative tritium signal intensities at δ 5.80 and 5.96 are consistent with expectations for an anti elimination of hydrogens from **7a**, assuming $k_H > k_D > k_T$ for loss of the C-3 hydrogen atom (cf. Scheme II).[19]

Figure 2b shows the ^{1}H-decoupled ^{3}H NMR spectrum of **3b** derived from the **7b** + **9b** isobutyrate mixture. Although the ^{3}H chemical shifts are not identical with those in Figure 1b [due to the presence of more Eu(fod)$_3$ in the solution], they correspond well with the relevant ^{1}H signals (Figure 2a). The intensity distribution of the two low-field ^{3}H signals complements that observed in Figure 1b. The two spectra, Figures 1b and 2b, require the conclusion that the dehydrogenation of isobutyryl CoA in this organism proceeds by antiperiplanar elimination of hydrogens from C-2 and C-3.[20] The stereochemistry thus parallels that observed for the dehydrogenation of *n*-butyryl CoA by short-chain acyl CoA dehydrogenase from pork liver,[21] and for the dehydrogenation of (2*S*)-2-methylbutyryl CoA in *Datura innoxia* plants.[22]

Acknowledgment. We express our thanks to Frank Shea and Professor Alan A. Jones, Clark University, Worcester, Massachusetts, for the ^{3}H NMR spectra. We also thank Dr. Eliahu Caspi for provision of hot lab facilities and for stimulating discussions. We thank Professor John A. Elvidge for provision of valuable information on tritium referencing procedures. The ^{3}H NMR spectra were recorded on an instrument supported in part by National Science Foundation Equipment Grant CHE77-09059. This work was supported by Grant GM 24420 from the National Institute of General Medical Sciences.

D. John Aberhart,* Chou-Hong Tann
Worcester Foundation for Experimental Biology
Shrewsbury, Massachusetts 01545

Received May 27, 1980

---

(17) ^{3}H NMR spectra were recorded at 95.9 MHz on a Bruker SXP 22/100 spectrometer. Samples were dissolved in ca. 0.4 mL of a mixture of CDCl$_3$ (90%) and Me$_4$Si (10%) and were sealed under N$_2$ in standard thin-wall 5-mm tubes. Tritium chemical shifts were determined relative to Me$_4$Si by the "ghost referencing technique".[8d] Spectra were run without NOE suppression to minimize spectrum acquisition time. The operation of NOE in the proton-decoupled spectra is expected to introduce only minor changes in *relative* signal intensities.[18] No apparent change in the *relative* intensities observed in Figure 1b was observed in the ^{1}H-*coupled* ^{3}H NMR spectrum of **3b** derived from **7a** + **9a** (see ref 19). However, the signal-to-noise ratio was substantially lower in the ^{1}H-coupled spectrum. The pattern appearing at ca. δ 4.5–5.0 (designated CF, Figures 1, 2) is the center frequency of the instrument and not a tritium resonance.

(18) Bloxsidge, J. P.; Elvidge, J. A.; Jones, J. R.; Ramachandra, B. M. *J. Chem. Res., Synop.* **1977**, 258–259. Cf.: Altman, L. J.; Silberman, N. *Steroids* **1977**, *29*, 557–565.

(19) The signal assignments are also supported, in part, by ^{1}H couplings observed in the proton-coupled ^{3}H NMR spectrum of **3b** derived from **7a** + **9a**. The δ 1.74 signal appeared as a doublet of doublets (J_1 = 7.7 Hz, J_2 = 13.4 Hz), due to vicinal coupling with the C-2 hydrogen and geminal coupling with the single ^{1}H on the chiral methyl group, respectively. The pattern shows that all residual methyl groups in the isolated **3a** (and therefore also in the starting material) which bear tritium also contain one deuterium atom. The peak at δ 5.80 appeared as a doublet (J = 6.6 Hz), supporting attachment of this tritium atom to carbon also bearing deuterium. Unfortunately, the tritium signal at δ 5.96 was only poorly resolved from background noise. Couplings of ^{3}H with ^{2}H could not be resolved in either the ^{1}H-coupled or the decoupled spectra.

(20) The results also support the involvement of a substantial isotope effect in the loss of the C-3 hydrogen.

(21) (a) Bücklers, L.; Umani-Ronchi, A.; Rêtey, J.; Arigoni, D. *Experientia* **1970**, *26*, 931–933. (b) Biellman, J. F.; Hirth, C. G. *FEBS Lett.* **1970**, *8*, 55–56. (c) *Ibid.* **1970**, *9*, 335–336.

(22) Hill, R. K.; Rhee, S.; Leete, E.; McGaw, B. A. "Abstracts of Papers", 178th National Meeting of the American Chemical Society, Washington, D.C., Sept 1979; Abstr. ORGN 023.

Angular Momentum, the Principle of Equal a Priori Probabilities, and "Intermolecular Entropy Corrections" in Equilibria of Ions and Molecules in the Gas Phase

Sir:

Two years ago, Lias and Ausloos[1] first suggested that the entropy term associated with gaseous equilibria of ions and neutral species may require a term to account for the effect of the long-range (r^{-4}) interaction between the two species even at pressures less than 1 torr. On the basis of a classical collision theory argument, they proposed[1-4] a pressure-independent correction term of a form deriving from collision frequencies (Z) in the forward and reverse directions (eq 1 and 2), where P designates

$$K_{eq} = (Z_f/Z_r)(P_f/P_r)\exp(-\Delta H/RT) = \exp(\Delta S/R - \Delta H/RT) \quad (1)$$

$$\Delta S = R\ln(Z_f/Z_r) + R\ln(P_f/P_r) = \Delta S_{int} + \Delta S_{stat} \quad (2)$$

the conventional "steric" factor. The first term on the right side of eq 2 is interpreted as an intermolecular entropy term (ΔS_{int}) and as a correction to the entropy (ΔS_{stat}) calculated on the basis of statistical mechanics. Various arguments against this proposal based on microscopic reversibility, transition-state theory,[5] and statistical mechanics have been offered, and the views of the proposers on these have been discussed extensively.[6] We present here an analysis employing a simple model system which demonstrates that at the low pressures (less than 1 torr) at which such equilibria are studied intermolecular correction terms based on the kinetic argument violate an elementary probability theorem and conservation of angular momentum; since such a term would have to apply to all systems, it cannot exist.

Thermodynamic expressions will contain a concentration-dependent intermolecular term, which may be derived by statistical considerations such as the well-known Debye–Hueckel treatment, at densities four or five orders of magnitude greater than the highest pressures used in experimental studies of ionic equilibria in the gas phase; these terms are not a subject of this communication.

We choose for demonstration a charge-transfer reaction (eq 3) between atomic species A and B of exactly equal ionization potentials and degeneracies but different polarizabilities, α_A and

$$A^+ + B = A + B^+ \quad (3)$$

α_B. The elementary, fundamental principle that all quantum states of equal energy have equal a priori probabilities underlies equipartition and all statistical mechanics; it requires without mathematical or further conceptual development that the equilibrium constant for reaction 3 is unity, $K_{stat} = 1$, at all temperatures, as long as the densities are sufficiently low so that the intermolecular interactions cannot affect the ionization potentials of A and B

---

(1) S. G. Lias and P. Ausloos, *J. Am. Chem. Soc.*, **99**, 4831 (1977).
(2) S. G. Lias, *Chem. Phys. Lett.*, **54**, 147 (1978).
(3) P. Ausloos and S. G. Lias, *J. Am. Chem. Soc.*, **100**, 1953 (1978).
(4) S. G. Lias and P. Ausloos, *J. Am. Chem. Soc.*, **100**, 6017 (1978).
(5) J. M. Jasinski, R. N. Rosenfeld, D. M. Golden, and J. I. Brauman, *J. Am. Chem. Soc.*, **101**, 2259 (1979).
(6) S. G. Lias, *NATO Adv. Study Inst. Ser., Ser. B*, **40**, 223 (1978).

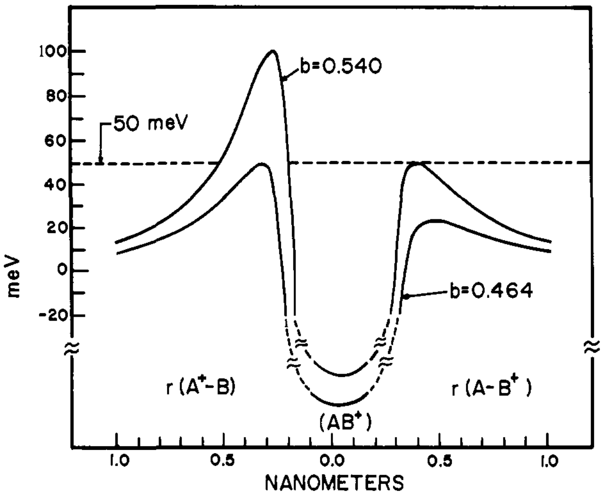


Figure 1. Effective potential for charge-transfer reactions $A^+ + B \rightleftarrows A + B^+$ at impact parameters of 0.540 nm (upper curve) and 0.454 nm (lower curve) when $\mu = 13.33$ au, $\alpha_A = 2\alpha_B = 10$ au, and $E = 50$ meV.

unequally.[7] The proposal of Ausloos and Lias,[1-4] however, leads to an equilibrium constant which must be corrected by the ratios of the forward and reverse collision frequencies. In the low temperature regime where all interactions except ion-induced dipole ones may be neglected, the collision frequencies are given by the polarization limit $Z_{A^+} = 2\pi e(\alpha_B/\mu)^{1/2}$ where e is the electronic charge and μ is the reduced mass of the system and is equal in both directions.[8] Since there is an equal probability for the charge to be on either species when the products separate, the equilibrium constant predicted by Ausloos and Lias is not unity but $K_{int} = {}^1/_2 Z_{A^+}/{}^1/_2 Z_{B^+} = (\alpha_B/\alpha_A)^{1/2}$ and $\Delta S = \Delta S_{int} = R \ln (\alpha_B/\alpha_A)^{1/2}$. The principle of equal a priori probabilities and the kinetic intermolecular correction are mutually exclusive.

The inclusion of such an intermolecular correction in this case also violates conservation of angular momentum. The dynamic model for ion-molecule reactions is well-established.[8-10] It may be applied to a charge-transfer reaction by restricting our demonstration system to one in which penetration of the centrifugal barrier (complex formation) is necessary for charge transfer, which should be the case at low temperatures. The description of an ion-molecule charge-transfer collision may then be based on defining the maximum angular momentum L_{max} (or the maximum impact parameter b_{max}) at a given energy for which capture may occur. That is, only those encounters between A^+ and B for which the kinetic energy E exceeds the entrance rotational barrier, $V_{rot\,in\,A^+} = L^4/(8\alpha_B e^2\mu^2)$, may lead to capture and therefore collision. Conversely, the kinetic energy determines the maximum angular momentum $L_m = (8\alpha_B e^2\mu^2 E)^{1/4}$, or maximum impact parameter, $b_{max} = [(2e^2\alpha_B)/E]^{1/4}$, for which collision may occur. This, however, defines only the collision frequency but does not speak of the number of encounters which may lead to products $A + B^+$. In order for these to be formed, the products must be able to separate, and this requires, of course,[11,12] that the (constant) energy exceed the rotation barrier in the exit direction $V_{rot\,exit\,B^+}$. Since α_B differs from α_A, $V_{rot\,exit\,B^+} = V_{rot\,in\,A^+}\alpha_A/\alpha_B$. When $\alpha_A = \alpha_B$ this is no problem in the forward direction because then the exit barrier is always smaller than the entrance barrier, but that is then not the case for the reverse reaction. Now $V_{rot\,exit\,A^+} = V_{rot\,in\,A^+}$ and the rate constant (rather than collision frequency) for the reverse reaction is exactly equal to the rate constant or collision frequency for the slower forward reaction. This is illustrated in Figure 1 which shows the effective potential V_e when $m_A = 40$ au, $m_B = 20$ au, $\alpha_A = 10$ au, $\alpha_B = 5$ au, and $E = 50$ meV for impact parameters of $b_{A^+} = 0.454$ and $b_{B^+} = 0.540$ nm, respectively. While impact parameters less than 0.454 nm permit charge exchange and complex formation in both directions, those between 0.454 and 0.540 au allow the formation of the collision complex from A and B^+, but the complex cannot penetrate the rotational exit barrier to A^+ and B, and the complex *must* redissociate to A and B^+. Therefore, $k_f/k_r = K = 1$, and $\Delta S_{int} = \Delta S = 0$, and not $R \ln (\alpha_A/\alpha_B)^{1/2}$ as required by the correction hypothesis. This simple, well-established dynamic argument, which is another expression of the principle of detailed balancing, clearly demonstrates that intermolecular entropy effects are excluded on the basis of simple physical laws alone. It is an interesting conclusion that the effective collision rates of the forward and reverse reactions in equilibria must be the same.

If A and B represent molecular entities, the matter is more complicated because the total angular momentum J is conserved, and the rotational distributions of reactants and products must be considered also. The formalism is now more complex and requires assumptions[5,12] which make the argument less stringent.

It remains to be understood why some experimental measurements appear to require a collisional correction to yield entropy data consistent with other information. It is possible that the experiments in question may not have been performed under true equilibrium conditions and that a kinetic component remained; when ions are sampled within 20 collisions of their formation,[13] the rate of formation in the reverse direction may become an influencing factor. Indeed, equilibrium measurements are also sensitive to relatively minor potential errors in the measurement of gas composition, mass-dependent ion-detector response, etc.[14]

Acknowledgment. The support of the Department of Energy under contract DEAS02-76-ERO-2567 is acknowledged gratefully.

---

[7] At low density, such a stabilization would be independent of the nature of the ion but dependent on density and composition because it corresponds to the integral over attraction terms with all neutrals in the system. Those should become unequal for the two ions only at densities approaching those of the condensed phase.

[8] G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).

[9] E. W. McDaniel, "Collision Phenomena in Ionized Gases", Wiley, New York, 1964, p 60 ff.

[10] M. Henchman, "Ion-Molecule Reactions", Vol. 1, J. L. Franklin, Ed., Plenum Press, New York, 1972, p 101.

[11] This limitation was first pointed out by H. M. Rosenstock, U.S. AEC Report JLI-650-3-T, TID-4500 (1959). It is a precursor of the phase space theory; J. C. Light, *J. Chem. Phys.*, **40**, 3321 (1964).

[12] G. G. Meisels, H. J. Weiss, G. M. L. Verboom, and T. Hsieh, *J. Am. Chem. Soc.*, **101**, 7189 (1979).

[13] S. G. Lias, private communication.

[14] A. J. Illies and G. G. Meisels, to be published.

G. G. Meisels
Department of Chemistry, University of Nebraska—Lincoln
Lincoln, Nebraska 68588

Received January 23, 1980

Facile Generation of a Reactive Palladium(II) Enolate Intermediate by the Decarboxylation of Palladium(II) β-Ketocarboxylate and Its Utilization in Allylic Acylation

Sir:

A reactive palladium(II)–enolate complex[1] is a useful reaction intermediate in organic synthesis.[2] Here we report a facile generation of the reactive palladium(II) enolate intermediate by the decarboxylation of a palladium(II)–β-ketocarboxylate complex under a mild condition and its utilization in allylic acylation. Thus, a catalytic amount of $Pd(PPh_3)_4$ induced the decarboxylation of allylic β-ketocarboxylates to produce α-allylic ketones via π-al-

---

[1] The palladium(II)–enolate complex may be formally expressed in three structures: palladium(II)–enolate, oxa-π-allylpalladium(II), and 2-oxoalkylpalladium(II) complexes. As sufficient information to discriminate these three structures is not presently available, we tentatively expressed it as the palladium(II)–enolate complex.

[2] Theissen, R. J. *J. Org. Chem.* **1971**, *36*, 752. Ito, Y.; Hirao, T.; Saegusa, T. *Ibid.* **1978**, *43*, 1011. Ito, Y.; Aoyama, H.; Hirao, T.; Mochizuki, A.; Saegusa, T. *J. Am. Chem. Soc.* **1979**, *101*, 494.

0002-7863/80/1502-6381$01.00/0