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NOTE ON PONDERAL EFFECTS IN EQUILIBRIA[*]

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The term "ponderal effect" was coined by Ingold and his co-workers (1) (in connection with entropies of activation in rate processes) for structural effects which depend "on the presence and distribution of mass". In a recent letter, Scott (2) has invoked the ponderal effect in a consideration of the trend in the equilibrium constants for the addition of HCN to para-alkyl benzaldehydes (~ 300°K)

$$RC_6H_4CHO + HCN \rightleftharpoons RC_6H_4CH(OH)CN \qquad (I)$$

The experimental finding that the equilibrium shifts progressively to the right with increasing mass of the alkyl group in the series R = Me, Et, i-Pr, t-Bu had previously been cited as evidence for hyperconjugation (3). Scott showed that the contribution of the translational partition functions to the equilibrium constants could alone account for about 40 per cent of the magnitude of the trend in the equilibrium constants as the R group is varied, and he concluded that the ponderal effect might well suffice to account for the complete trend in K if it were also possible to evaluate the contribution of the rotational partition functions. While Baker (3) explicitly defined his equilibrium constant in terms of reactant concentrations divided by product concentration in eq. (I), Scott mistakenly

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assumed that the equilibrium constant referred to the common present usage which is also employed here (*i.e.*, product/reactants). Thus, the direction of the translational partition function effect is opposite to the trend found in the observed equilibrium constants.

Scott's considerations do nevertheless pose an interesting question with respect to equilibria such as (I). Suppose that the electronic energy difference between product and reactants is independent of R. Suppose also that the internal coordinates of each molecular species which contains the R group (R-Reac and R-Prod) can be divided into two sets, i) the substituent coordinates and ii) the framework coordinates, so that the following conditions are satisfied. The same set of substituent coordinates is to be associated with all species containing a given R group. The same set of framework coordinates is to be associated with all the reactants and another set with all the products. The properties* of the R set of substituent coordinates are the same in the reactant containing the R group, R-Reac, and in the corresponding product, R-Prod.** The properties of the reactant set of framework coordinates are the same in all reactants (R-Reac, R'-Reac, *etc.*); the properties of the product set of framework coordinates are the same in all products.*** Under these circumstances,

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[*] The harmonic potential energy surface for the vibrational motion of the nuclei in a molecule is defined in terms of the force constants and the corresponding displacements of the internal coordinates from their equilibrium configurations. The expression "properties of a set of coordinates" refers to the equilibrium configurations of these coordinates, the masses of the atoms which define these coordinates, and the values of the force constants which correspond to motion in only this set of coordinates. A non-vanishing interaction force constant between a framework coordinate and a substituent coordinate is considered a property of either (but not of both) of the sets of coordinates.

[**] For interaction force constants between framework and substituent coordinates, which are considered properties of the substituent coordinates, this statement implies that such force constants are permitted only with those framework coordinates with the same configurational properties and the same atomic masses in both reactant and product.

[***] Similar considerations, as in the preceding footnote, apply for the interaction force constants between framework and substituent coordinates, which are considered properties of the framework coordinates.

does the equilibrium constant depend on R? Such a dependence will be denoted as a pure ponderal effect. The pure ponderal effect conditions appear appropriate for describing an actual situation in which the R group is attached to the reactant at some distance from the main reaction site and in which R does not affect the equilibrium through either an electronic or a steric effect. The evaluation of the pure ponderal effect contribution to a trend in equilibrium constants is complicated by a lack of precise knowledge of the proper geometries and especially of the proper force constants to be used for the respective molecules, particularly if effects besides the pure ponderal effect are of importance. The subsequent discussion of some actual calculations demonstrates the present approach to this problem.

An isotope effect is a type of ponderal effect. It is well known that statistical mechanical consideration of isotope effects only in terms of masses and moments of inertia (translations and rotations), without consideration of vibrations, may lead to erroneous conclusions. It can be shown that equilibrium isotope effects vanish in the classical limit and that they are, therefore, quantum mechanical effects. The first order quantum mechanical contribution to the isotope effect also vanishes if the force constants and other properties for coordinates involving the isotopically substituted position do not change between reactant and product (4). Isotope effects under such circumstances will be referred to as "no force constant change" isotope effects; they are pure ponderal effects. The classical limit corresponds to the very high temperature limit. The first quantum approximation is the correct expression at somewhat lower temperatures but is not necessarily adequate at room temperature. Explicit calculations (4) have, however, shown that "no force constant change" isotope effects are quite small in the room temperature region, even for hydrogen isotopes (*i.e.*, $K_H/K_D \simeq 1.0$). For more general mass effects (such as replacement of $-CH_3$ by $-C_2H_5$), it can be shown, with the use of statistical mechanical methods, that the pure ponderal effect conditions almost suffice[*] to make both the classical contribution and the first order quantum mechanical contribution to the equilibrium constant independent of the nature of the R group. This analogy of the more general pure ponderal effects to "no force constant change" isotope effects leads one to suspect that the former may also be quite small in the room temperature region. Explicit calculations on model systems were therefore undertaken.

When one carries out calculations for a model system, the conclusions apply strictly only to that particular system. Calculations are now presented for the model equilibrium

$$\text{R-C-C-C-C-CHO} + \text{HCN} \rightleftharpoons \text{R-C-C-C-C-CH(OH)CN} \qquad \text{(II)}$$

R = Me, Et. Calculations on other equilibria, which have led to similar conclusions, will not be presented here although these calculations certainly strengthen the feeling that the over-all conclusion is correct. Equilibrium (II) is used as a simplified model for equilibrium (I). The ponderal effect on the translational partition functions for (II) is actually larger than for (I).

The statistical mechanical calculations of pure ponderal effects involve the computation of all the normal vibrational frequencies

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[*] The pure ponderal effect conditions do suffice for the first quantum contribution. For the classical limit, there are two additional conditions (which are sufficient but not always necessary). Those framework coordinates which have atoms in common with substituent coordinates must appear both in the reactant set and in the product set with the same equilibrium configurations. (An alternative form of this condition involves those substituent coordinates which have atoms in common with framework coordinates.) All interaction force constants between a non-redundant substituent coordinate and a non-redundant framework coordinate must be zero. The first condition will usually be satisfied in a pure ponderal effect situation if the substitution is far removed from the reaction site. As for the second condition, the reference to non-redundant coordinates should lead to no additional complication with proper choice of substituent and framework coordinates. Since force fields without interaction force constants are reasonably good approximations (valence force approximation), one would not expect the lack of fulfillment of this condition in an actual situation to lead to large deviations.

corresponding to the force constants and geometries assumed for the relevant aldehydes and cyanohydrins. Such calculations are feasible only with large digital computers; the present calculations were carried out (assuming harmonic vibrational frequencies) on an IBM 7094 computer with the same programs (based on frequency calculation programs kindly furnished by Dr. J. H. Schachtschneider) previously employed for isotope effect calculations.[*] As for isotope effects (5), the ponderal effects on equilibria can be divided into three multiplicative terms: 1) the mass-moment of inertia factor resulting from the translational and rotational partition functions, 2) the excitation factor resulting from the thermal excitation of vibrations, and 3) the zero-point energy factor resulting from the vibrational zero-point energies.

Force constants and geometries for aldehydes and cyanohydrins in (II) were chosen so that the conditions for a pure ponderal effect are satisfied. Force constant and geometry changes between aldehyde and corresponding cyanohydrin were taken to occur only[**] for coordinates which contain atoms at the reaction site, $-CHO + HCN \rightleftharpoons -CH(OH)CN$; changes between the methyl and the corresponding ethyl compound were taken to occur only[***] for coordinates which contain atoms in the alkyl groups. Reasonable values were chosen for bond distances and bond angles; a detailed description of geometries will not be given here.[****] In the calculation designated as

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[*] As is usual, solvation differences are ignored and the statistical mechanical calculations are made for the gas phase. The degrees of freedom for the nuclear motions of each N atomic molecule are 3 classical translations, 3 classical rotations, and 3N-6 quantized vibrations.

[**] Some calculations, which will not be explicitly reported here, were also carried out in which certain force constant and geometry changes were made closer to the point where the R group attaches to the molecular skeleton. With not too violent changes close to R and with the conditions for pure ponderal effects still met, these calculations lead to the same conclusions as those reported here.

[***] Similar comments, as in the preceding footnote, apply here.

[****] All the C-C-C angles were taken as tetrahedral.

Case A in Table I, reasonable values were used for all force constants, including interaction force constants.* It is assumed that force constants and geometries corresponding to given coordinates are transferable from molecule to molecule; thus the reasonable values above were taken, where available, from analyses on other molecular systems. With the alkyl group so distant from the reaction site, a number of coordinates can be classified both as framework coordinates and as substituent coordinates. These force constants and geometries are reasonable for investigating the pure ponderal effect but they cannot be described as the "best" ones for these molecules. Since one expects large pure ponderal effects when force constants tend to infinity, a second set of calculations (Case B) is presented for unreasonably "stiff" molecules (with the same geometries as above). Here all force constants in reactants and products, except interaction force constants, have been set equal to 10.0 units (millidyne/Å for stretches and millidyne Å for bends) and all those interaction force constants which are non-zero in Case A have been set equal to 2.0 units.

The equilibrium constant ratios are presented in Table I. In both cases, the classical ratio deviates from unity by less than one part in ten thousand and the first quantum contribution vanishes. Except at quite low temperatures, there is no (within limits) ponderal effect [K(methyl)/K(ethyl) = unity], even for the stiff molecules. The absence of ponderal effect results from a cancellation; the mass-moment of inertia factor by itself is quite sizable. It is also interesting that the low temperature effect here is actually in the opposite direction from unity to that of the mass-moment of inertia factor.

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* Interaction force constants between coordinates which are far separated were generally set equal to zero.

TABLE I

K(Methyl)/K(Ethyl)

	T(°K)	Mass-Moment of inertia factor	Excitation factor	Zero-point energy factor	$\frac{K(Me)}{K(Et)}$
Case A	10	1.1704	0.9977	0.7055	0.8240
	100	1.1704	0.8847	0.9657	0.9999
	200	1.1704	0.8695	0.9827	1.0000
	300	1.1704	0.8644	0.9884	1.0000
	400	1.1704	0.8619	0.9913	1.0000
Case B	100	1.1704	0.9875	0.7986	0.9230
	200	1.1704	0.9481	0.8936	0.9916
	300	1.1704	0.9200	0.9278	0.9990
	400	1.1704	0.9037	0.9453	0.9998

Thus, the effect on an equilibrium of the substitution of various alkyl groups at some distance from the reaction site under pure ponderal effect conditions bears great similarity to a "no force constant change" isotope effect. It is generally not correct to invoke a pure mass effect (*i.e.*, a pure ponderal effect) as an important factor in a consideration of the effect of various alkyl substituents on an equilibrium such as (I), at room temperature and above.[*]

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[*] For reaction rates, one finds under similar circumstances, with transition state (in rate) substituted for product (in equilibrium), that the relative rates are given by the ratio of the imaginary frequencies (*i.e.*, the so-called decomposition frequencies) in the transition state.

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